RECOVERY OF SILVER FROM ZINC PLANT RESIDUES
PHASE II

FINAL REPORT

by

NORANDA INC.
Pointe Claire, Quebec

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada

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CANMET Scientific Authority : J.E. Dutrizac

noranda

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J.Y. Kim
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ABSTRACT

This report describes an investigation of the feasibility of recovering silver in electrolytic zinc plants by flotation of calcine and leach plant residues.

Calcine leaching studies and flotation testwork carried out by Noranda Research Centre to characterize the effect of zinc plant leach conditions on silver floatability and to determine the effect of plant operating requirements, with respect to residue thickening and washing, on the flotation of silver are reported. It is shown that whereas flotation of silver from calcine is not attractive, recovery of silver from neutral leach residues produced under slightly acidic conditions, so as to avoid iron hydrolysis, is technically viable and merits consideration. Unwanted precipitation of iron during the neutral leach depresses silver recovery and grade, and restoration of floatability requires that the residue be subjected to a high acid leach step.

The rate of silver flotation is shown to be slow, and long roughing times are required. Residue washing is also required to control the ionic strength of the flotation medium and to avoid losses in flotation selectivity. Flocculants suitable for residue thickening do not affect silver selectivity or grade, however, provided the flotation feed is first subjected to high shear repulping.

Conclusions and a discussion of factors to be considered during integration of a flotation process into an electrolytic zinc plant are given.

RÉSUMÉ

Ce rapport traite d'une étude de faisabilité portant sur la récupération de l'argent par flottation de calcinés ou de résidus de lixiviation dans les usines à électrolyse de zinc.

On y présente les résultats des études portant sur la lixiviation de calcinés ainsi que sur les essais de flottation effectués par le Centre de recherche Noranda dans le but de caractériser les effets des conditions de lixiviation utilisées dans une usine de zinc sur la capacité de flottation de l'argent et pour déterminer les conséquences des exigences fonctionnelles de l'usine en ce qui concerne l'épaississement et le lavage des résidus sur cette même flottation de l'argent. Il est démontré que la flottation de l'argent à partir des calcinés ne saurait devenir une alternative intéressante at qu'il est techniquement possible et préférable d'effectuer la flottation de ce métal à partir de résidus neutres de lixiviation produits sous des conditions légèrement acides et ce, afin d'éviter l'hydrolyse du fer. En effet, la précipitation du fer durant la lixiviation neutre est à éviter puisqu'elle réduit la récupération ainsi que la teneur en argent du concentré obtenu. Le rétablissement de la capacité de flottation requiert que le résidu soit soumis à une étape de lixiviation à haute acidité.

Il est également démontré que la flottation de l'argent est un processus lent, requérant de longues périodes de dégrossissage. Le lavage des résidus est aussi requis pour contrôler la force ionique de médium de flottation et pour éviter la perte de sélectivité en flottation. Les agents de floculation utilisée pour l'épaississement des résidus n'ont aucume conséquence sur la sélectivité pour l'argent ni sur sa qualité en autant que l'alimentation de la flottation soit d'abord soumise à une pulvérisation intense.

Une discussion des facteurs devant être pris en considération pour ce qui est de l'intégration d'un procédé de flottation par une usine de zinc s'ensuit et le rapport se termine avec conclusions.

SUMMARY

1. Silver recoveries in Canadian zinc plants range from 0% at Canadian Electrolytic Zinc (jarosite conversion process) and Kidd Creek (one-stage jarosite process) to >90% at Cominco and Hudson Bay, where the neutral leach residues are fed to either a lead blast furnace (Cominco) or a copper reverberatory furnace (Hudson Bay). One of these plants (CEZ) has an accumulation of 800,000 tons of residue containing ∿6 opt Ag, produced prior to the introduction of jarosite technology, in storage ponds. There is thus considerable scope for improvement in the recovery of silver in the Canadian zinc industry.

   This report presents the results of an experimental program conducted to examine the effect of zinc plant leach conditions on the floatability of silver in the resulting leach residues, and to determine the requirements for recovery of silver by flotation.

2. Flotation of neutral leach residue (pH 1.5) has been found to be technically viable and merits consideration for those plants, without a high acid leach circuit, having significant silver values in the feed. Leach conditions must be kept slightly acid in the early stages of the neutral leach to promote the formation of Ag_2S, $(Ag,Cu)_2S$ and Ag_2S rims on unroasted sphalerite, while simultaneously avoiding the hydrolysis of soluble iron which depresses silver recovery and grade. The flotation is slow and long roughing times are required.

3. Under the preferred conditions, locked cycle flotation tests (roughing and two stages of cleaning) with a sample of pH 1.5 neutral leach residue produced from CEZ calcine, in which the leach residue (24.0% Zn, 8.9% Pb, 1.5% $S^=$, 0.036% Ag) was flocculated with Percol 351, filtered, washed, repulped at high shear, and floated in diluted leach liquor (34 g/L Zn, 0.5 g/L Fe, 0.9 g/L Mn, 0.1 g/L Cu, pH 1.9) with dithiophosphate (R-3501) and thionocarbamate (S-4037), resulted in 83% silver recovery to a concentrate assaying 0.5% Ag, 3.6% Pb and

39.0% Zn. The flotation concentrate (5.9 wt % of residue feed) contained most of the unroasted sphalerite in the residue feed.

4. Flotation of washed neutral leach residues, produced by leaching calcine from Kidd Creek and two overseas zinc plants at pH 1.5 in a pilot plant, resulted in silver recoveries of 57-88% to twice-cleaned concentrates assaying 0.9-2.3% Ag.

5. Flotation of silver from neutral leach residue produced at pH 1.5 cannot be conducted directly in zinc electrolyte, and requires that the residue be thickened and partially washed prior to flotation to avoid the loss of silver selectivity that has been encountered during flotation in media containing high levels of zinc electrolyte (>30 g/L Zn). Flocculants suitable for residue thickening do not adversely affect silver flotation provided the residue is subjected to high shear repulping prior to silver flotation.

6. Flotation of silver from neutral leach residues produced at pH 4, such as those typically encountered in the last stage of a neutral leach circuit, was poor. Concentrate grades were only 0.2-0.4% Ag at 25-35% silver recovery. The poor silver floatability is believed to be due to fouling of the silver by precipitation of iron and other metals during neutralization of the leach liquor to pH 4.

7. The floatability of silver contained in neutral leach residues produced at pH 4 can be largely restored by subjecting the residue to a hot acid leach at 95°C and 100 g/L H_2SO_4 for 6 h. A low acid leach at pH 1.5, such as might be employed to dissolve excess zinc oxide from the residue prior to the hot acid leach, is insufficient to overcome the damage caused in the neutral leach at pH 4.

8. The floatability of silver contained in samples of CEZ and Kidd Creek calcines was found to be poor, and attempts to improve the floatability by conditioning the calcine with a silver "collector", such as sphalerite, were unsuccessful.

9. Attempts to float silver from samples of CEZ pond residue (14-20% Zn, 0.02-0.03% Ag), produced before the adoption of jarosite technology, were unsuccessful (<20% Ag recovery). Furthermore, mild acid treatment of the residue prior to flotation was not effective in cleaning surfaces and/or liberating silver in a floatable form.

10. Work is required to assess the integration of neutral leach residue flotation into an existing plant, and to demonstrate the flotation at the pilot scale using actual plant residues. This work would define any required leach circuit modifications, liquid-solid separation requirements, process water requirements, allowable electrolyte levels in the flotation medium, sensitivity of silver flotation to process upsets in the leach plant, flotation circuit operating characteristics, and data required for final process design.

1. INTRODUCTION

Canada is the world's largest supplier of zinc concentrates and one of the major producers of zinc metal. Typical Canadian zinc concentrates contain 1-3 opt Ag, so that the silver input to a roast-leach-electrowin plant treating 250,000-400,000 tpy of concentrate ($\sim$100-200,000 tpy Zn) amounts to 250,000-1,200,000 oz per year, with a current value of $3-11 M.

Silver recoveries in Canadian zinc plants range from 0% at Canadian Electrolytic Zinc (jarosite conversion process) and Kidd Creek (one-stage jarosite process) to >90% at Cominco and Hudson Bay, where the neutral leach residues are fed to either a lead blast furnace (Cominco) or a copper reverberatory furnace (Hudson Bay). One of the Canadian zinc plants (CEZ) has an accumulation of 800,000 tons of residue, produced prior to the introduction of jarosite technology, in storage ponds. These residues contain $\sim$6 opt Ag, with a current value of $40-45 M.

It is apparent from the above that there is scope for improvement in the recovery of silver in the zinc industry, and this improvement will be required, in the face of rising silver prices, for Canadian zinc plants to maintain their competitive position as producers of zinc metal. Lack of silver recovery technology, not only reduces potential revenues, but can weaken the position of an electrolytic zinc plant in the zinc concentrate market where it can be competitive only in the purchase of low silver-containing concentrates.

Work(1) conducted previously by Noranda Research Centre with CANMET support (DSS contract 1SQ 83-0009) critically reviewed both the literature and plant practice in the flotation of silver from zinc plant residues, and examined the fundamental floatability of naturally occurring silver minerals which might be contained in actual zinc plant residues. This work demonstrated that argentite (Ag_2S), cerargyrite (AgCl) and native silver can be readily floated with sulphide collectors under acidic conditions such as those used for the treatment of leach residues. The flotation response of silver from actual CEZ and Kidd Creek residues, however, varied widely (8-80% recovery), depending on the source of the residue and the conditions under which it was produced. It was concluded that the successful flotation of silver from residue requires a good knowledge of the effect of the leach chemistry on the form and occurrence of silver in the residue, and that plant leach conditions must be controlled and/or modified to maintain silver in a liberated and floatable form.

In view of the technical and economic potential of flotation to recover silver from zinc leach residues, CANMET awarded a second contract to Noranda Inc. to develop further residue flotation technology. The objectives were:

(i) to characterize the effect of zinc plant leach conditions on the floatability of silver in zinc plant residues

(ii) to determine the effect of zinc plant operating requirements, with respect to residue thickening and washing, on the flotation of silver from residue produced under optimum leach conditions

(iii) to determine the potential for silver recovery in Canada by flotation of zinc plant residue, and to comment on any pilot scale testwork required.

2. FLOTATION OF CALCINE

Zinc calcine, produced by roasting zinc concentrates at ~960°C to eliminate sulphide sulphur, is the principal feed to the hydrometallurgical circuit of a roast-leach-electrowin plant and the source of the silver input. Flotation of silver from calcine, if feasible, could avoid leach circuit modifications that may well be necessitated by residue flotation and/or provide a means of silver recovery that would be independent of the circuit flowsheet employed for iron elimination. Furthermore, examination of the floatability of silver contained in calcine could provide indirect evidence of changes in the form of silver from calcine through the various residues produced in a zinc circuit.

2.1 Samples and Procedure

The flotation studies were conducted with as-received samples of calcine (Table I) from both Canadian Electrolytic Zinc (CEZ) and Kidd Creek Mines (KCM). Experimentally, 500 g of calcine were slurried with water at about 25% solids and conditioned with 100 g/tonne R-3501 (dithiophosphate) and 50 g/tonne S-4037 (thionocarbamate) for 10 min. at the natural pH (~6.0). Flotation was carried out with frother AF 65, and four 5-minute cuts were taken during a 20-minute rougher flotation period for silver and zinc analyses. In certain tests, the calcine was conditioned with zinc sulphide prior to collector conditioning in an attempt to "sulphidize" the silver and render it floatable by formation of silver sulphide rims on the zinc sulphide surface. Variables investigated during sulphide conditioning were the source of the zinc sulphide, conditioning time (30 or 120 min.) conditioning temperature (20°C or 65°C), and weight of zinc sulphide addition (1-6% of calcine).

The zinc sulphide samples employed were sphalerite concentrate from Brunswick Mining, sphalerite concentrate from Pine Point Mines, a pure sphalerite mineral specimen, reagent-grade zinc sulphide and freshly precipitated zinc sulphide (Table I).

TABLE I

CHEMICAL ANALYSIS OF CALCINE AND ZnS SAMPLES

Samples	Assays, %					
	Zn	Ag	Fe	Pb	S_T	$S^=$
CALCINE SAMPLES						
CEZ - Calcine (I)	59.4	0.012	9.89	2.00	-	-
CEZ - Calcine (II)	61.1	0.01	12.0	2.41	-	-
Kidd Creek Calcine	61.8	0.013	11.6	0.94	-	-
ZnS Samples						
Brunswick Zn Conc. 92% minus 400 mesh	53.5	0.01	9.23	1.44	33.5	32.9
Pine Point Zn Conc. 37% minus 400 mesh	65.2	<0.002	2.75	1.42	-	-
Mineral Specimen[1] 100% minus 400 mesh	65.5	<0.002	0.35	-	32.8	-
Reagent Grade ZnS	67.1	-	-	-	32.9	-
Precipitated ZnS[2] 100% minus 10 microns	60.5	-	-	-	30.1	-

[1] Mineral specimen from Elmwood Mines, Tenn., U.S.A. yellowish powder.

[2] ZnS was precipitated by reacting $ZnSO_4$ solution with Na_2S solution for 30-min. at 75°C, filtering and washing the precipitate with hot distilled water(1).

2.2 Results and Discussion

The floatability of the silver contained in the CEZ and Kidd Creek calcine samples is poor. Whereas recoveries were generally improved by conditioning with sulphides, the silver recoveries in all tests were less than 40% in roughing (Figures 1 to 6). Rougher concentrate grades were only 2-3 times the head grades, indicating no significant improvement in silver selectivity.

The relative effectiveness of the various sulphides as conditioning reagents is difficult to define due to the overall poor results, but there is some indication that the pure sphalerite mineral was the most effective.

The reason for the overall failure of the sulphides to enhance the floatability of silver contained in calcine cannot be defined, but may be due to the high pH (∿6) in conditioning. Silver has been found to react with sphalerite under acidic conditions, and flotation concentrates produced from neutral leach residues in the previous study([1,2]) contained large amounts of silver sulphide rimmed on sphalerite. Recently, a U.S. Patent was granted([3]) to Societe Miniere et Metallurgique de Penarroya on the use of zinc sulphide to recover silver from sulphate solutions by reaction at a pH between 1 and 4. Reduction of the pH from ∿6 to the range 1-4 is not feasible during conditioning of calcine with sphalerite due to the high acid consumption by the calcine.

2.3 Conclusion

The silver contained in the zinc calcine samples from CEZ and Kidd Creek is not amenable to direct recovery by flotation, and conditioning of the calcine with various zinc sulphide materials prior to flotation is not effective.

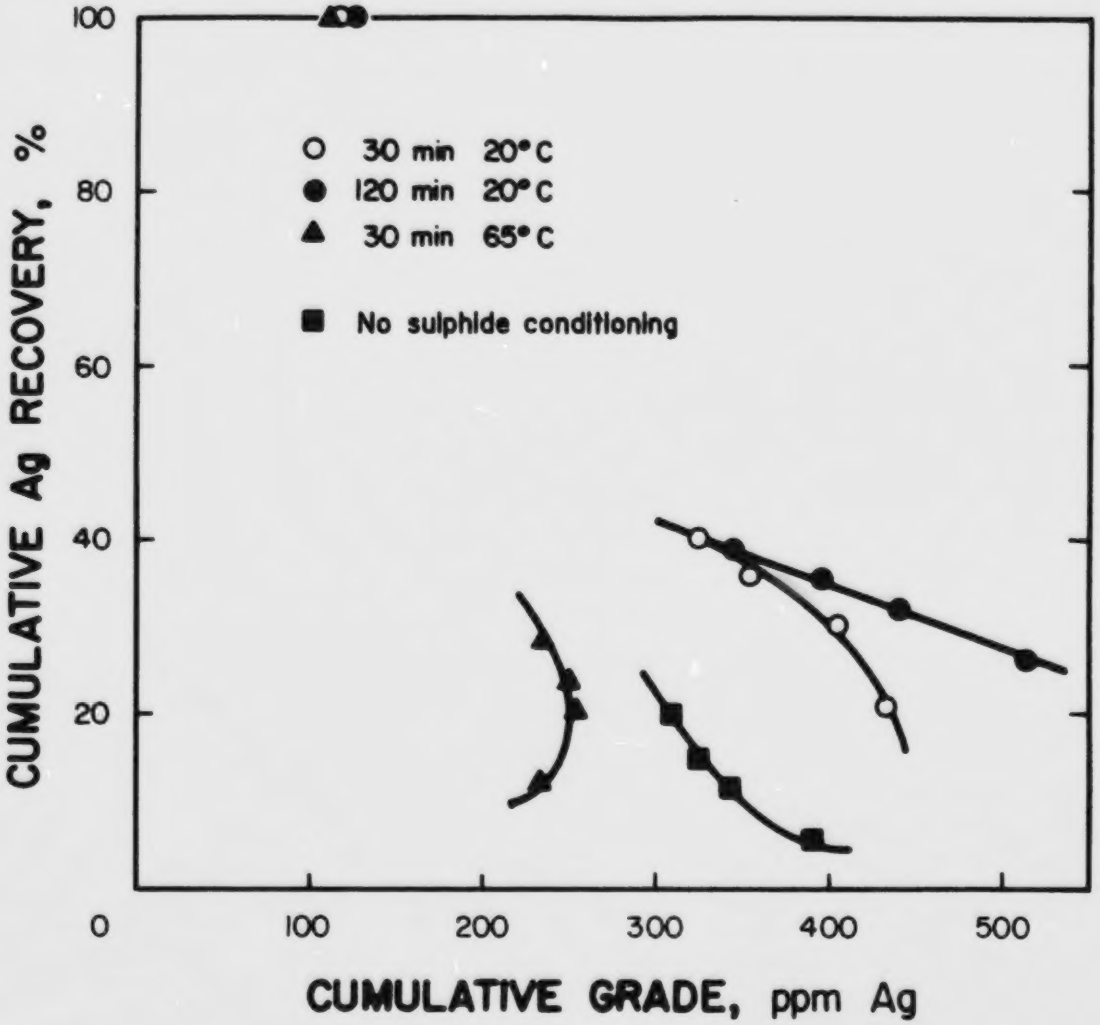

Figure 1. Effect of conditioning CEZ calcine I with Brunswick zinc concentrate (3% by weight of calcine) on silver grade-recovery during rougher flotation.

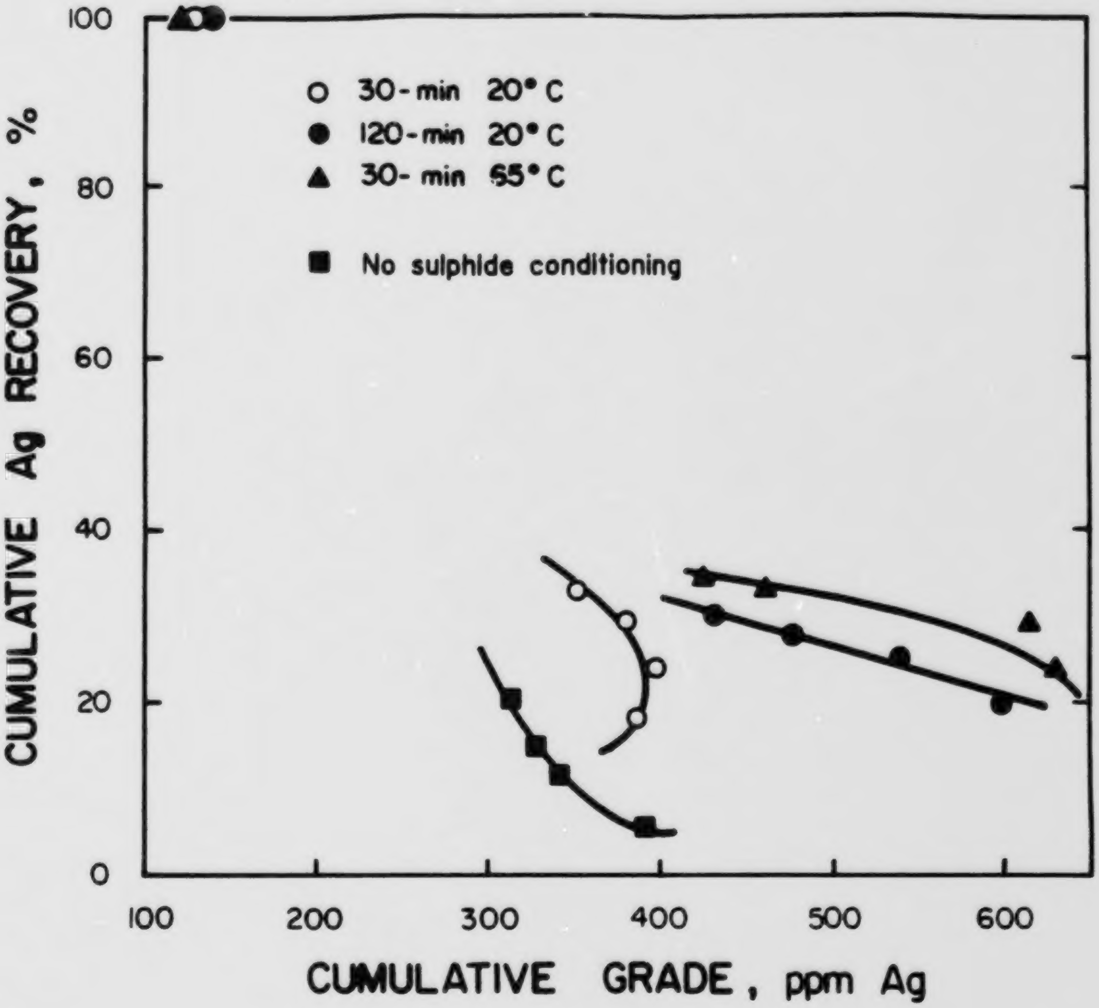

Figure 2. Effect of conditioning CEZ calcine I with pure ZnS mineral (3% by weight of calcine) on silver grade-recovery during rougher flotation.

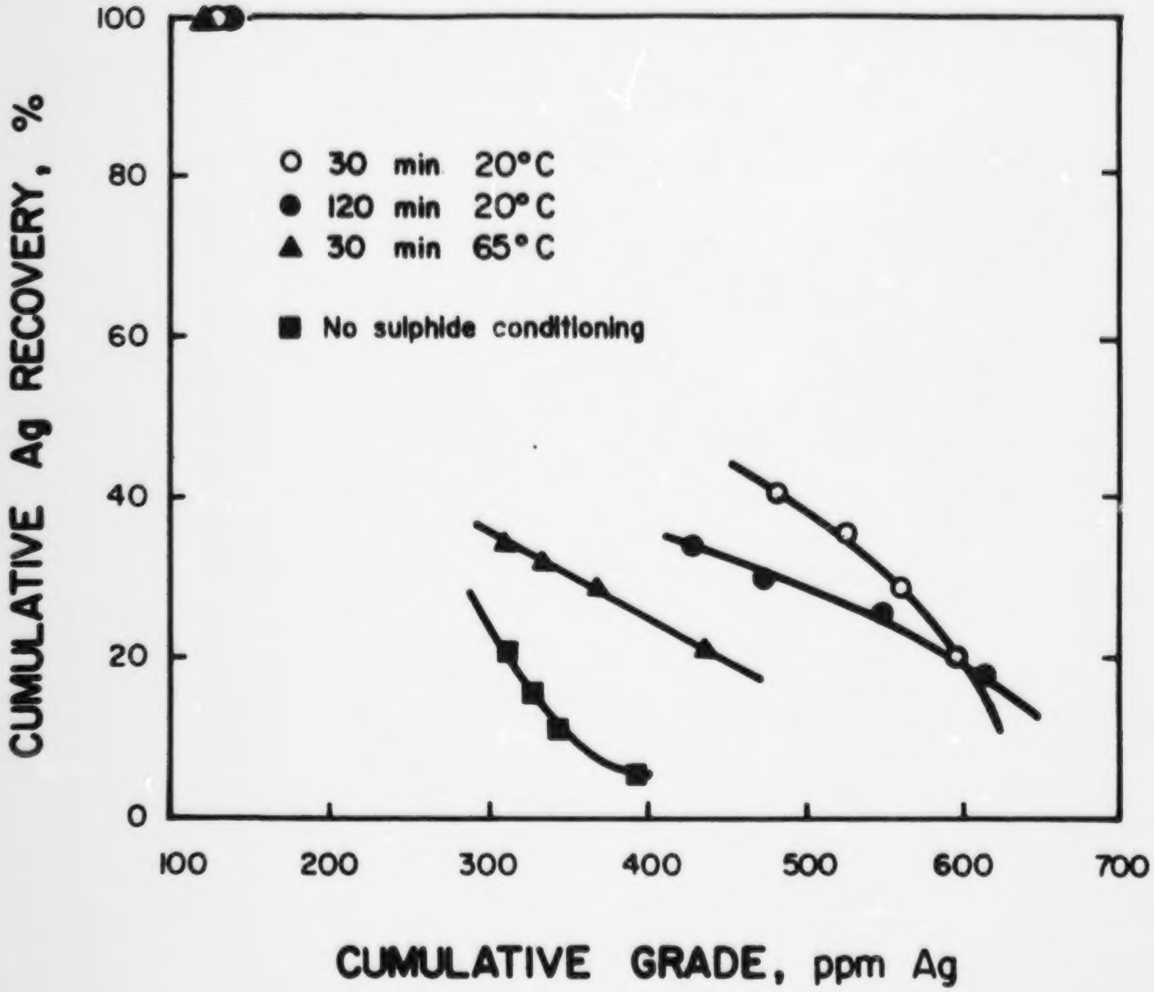

Figure 3. **Effect of conditioning CEZ calcine I with** reagent grade ZnS **(3% by weight of calcine) on silver grade-recovery during rougher** flotation.

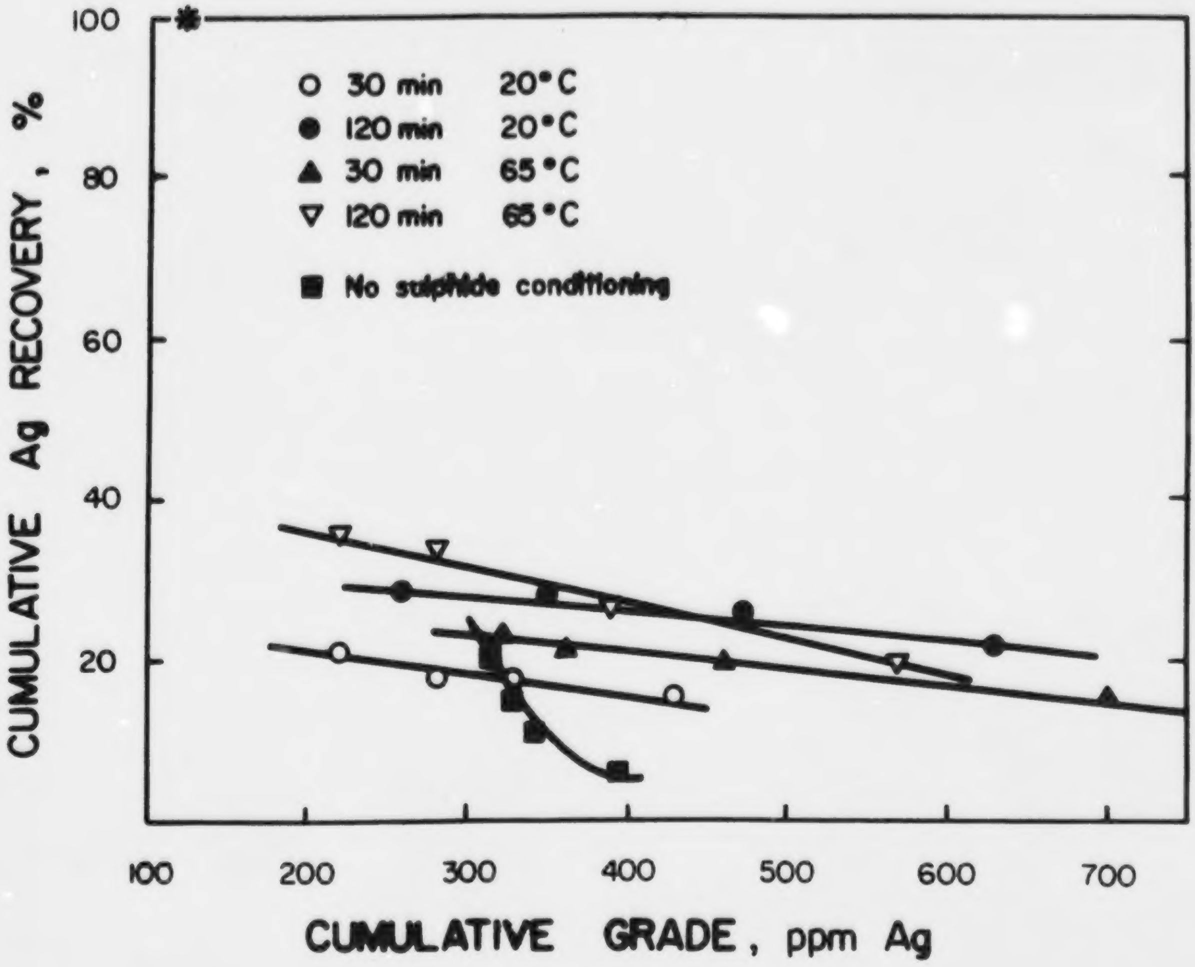

Figure 4. Effect of conditioning CEZ calcine I with freshly precipitated ZnS (3% by weight of calcine) on silver grade-recovery during rougher flotation.

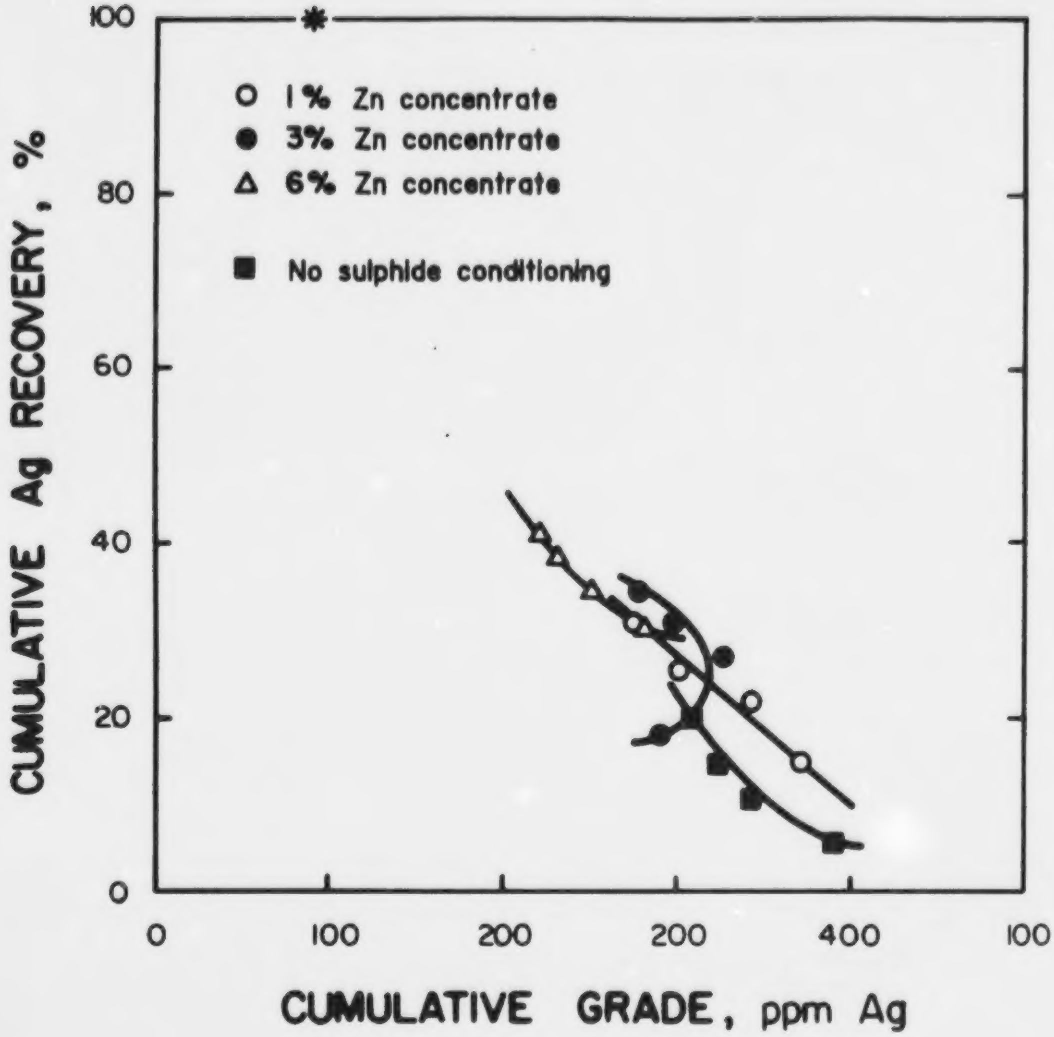

Figure 5. Effect of conditioning CEZ calcine II with Pine Point concentrate for 30 min. at 20°C on silver grade-recovery during rougher flotation

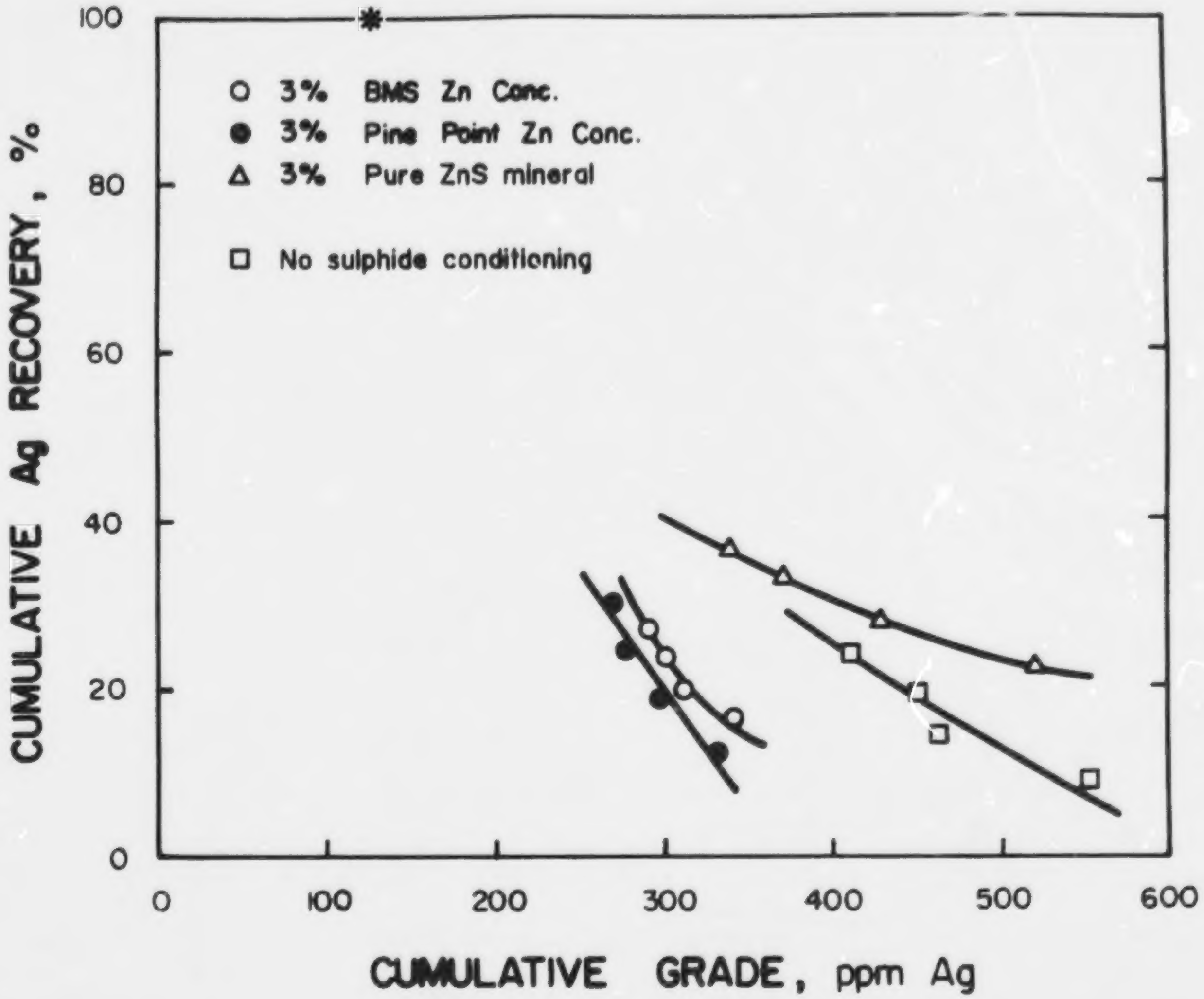

Figure 6. Effect of conditioning Kidd Creek calcine with various sulphides at 20°C for 30 min. on silver grade-recovery during rougher flotation.

3. FLOTATION OF CEZ POND RESIDUE

3.1 Introduction

In the previous contract study(1), roughing and cleaning flotation studies with a sample of CEZ pond residue (0.023% Ag, 0.5% Pb, 20.1% Zn, 36.6% Fe, 2.1% S) produced before the adoption of jarosite technology and using a variety of collectors at pH 3-5, resulted in silver recoveries of 42-46% to twice-cleaned concentrates assaying 0.31-0.39% Ag, 0.06-0.08% Pb, 59-63% Zn and 6-9% Fe. The best results (0.39% Ag grade, 46% Ag recovery) with this oxidized and aged material were obtained by flotation with mercaptobenzothiazol (R-404) at pH 3.0.

Mineralogical examination(1,2) of the pond residue feed sample and the corresponding flotation concentrate showed that the residue consisted of zinc ferrite, sphalerite, quartz and hematite, often cemented together by an amorphous iron hydroxide phase. The flotation concentrate contained sphalerite rimmed with Ag_2S and $(Cu,Ag)_2S$; inclusions of these sulphides were also detected in some of the larger sphalerite grains.

In view of the identification of the cementing iron hydroxide phase and the value of the silver in pond residue, a limited pond residue flotation study was undertaken to evaluate (i) acid pretreatment of the residue, to dissolve some oxidic phases prior to flotation, and (ii) sulphidization/conditioning of the flotation feed with Na_2S or zinc concentrate.

3.2 Samples and Procedure

Samples of wet residue from Ponds I and II at CEZ were dried at room temperature, and screened to minus 10 mesh to remove coarse material. The chemical and size analyses for each minus 10 mesh sample are given in Tables II and III, respectively.

TABLE II

CHEMICAL ANALYSIS OF CEZ POND RESIDUE SAMPLES

Residue	Assay, %						
	Ag	Zn	Fe	Cu	Pb	$S(SO_4^=)$	$S^=$
Pond I	0.023	19.4	37.2	1.06	0.93	2.12	0.30
Pond II	0.015	14.7	34.8	1.02	0.70	4.58	0.56

TABLE III

SIZE ANALYSIS OF CEZ POND RESIDUE SAMPLES[1]

Size Fraction Mesh	Wt.%	Assay, %				Distribution, %			
		Ag	Zn	Fe	Pb	Ag	Zn	Fe	Pb
POND I RESIDUE									
+200	2.9	0.021	14.5	27.9	0.70	2.2	2.2	2.1	2.1
200/270	3.3	0.017	15.0	35.7	0.52	2.1	2.5	3.1	1.8
270/400	3.8	0.025	16.2	39.2	0.49	3.5	3.2	4.0	1.9
-400	90.0	0.028	19.9	37.9	1.02	92.2	92.1	90.8	94.2
Total	100.0	0.027	19.4	37.6	0.97	100.0	100.0	100.0	100.0
POND II RESIDUE									
+200	7.1	0.012	15.9	30.3	0.70	3.8	8.2	6.2	7.1
200/270	7.0	0.012	16.5	37.2	0.38	3.8	8.4	7.5	3.8
270/400	7.1	0.023	16.8	38.6	0.29	7.3	8.6	7.8	2.9
-400	78.8	0.024	13.1	34.7	0.77	85.1	74.8	78.5	86.2
Total	100.0	0.022	13.8	34.8	0.71	100.0	100.0	100.0	100.0

[1] Screened to minus 10 mesh to remove foreign matter.

A series of 30-min. flotation rate studies was conducted with Pond I residue that had been subjected to various degrees of acid pretreatment and sulphidization. In the initial tests, 1 kg of residue was slurried at 30% solids and conditioned at 20°C and pH 1.0 or 3.0 for 10 min. The pulp was then further conditioned for 10 min. with 100 g/tonne $Na_2S \cdot 9H_2O$ (40% of stoichiometric for contained Ag) and/or 30 g of Brunswick zinc concentrate, prior to a final 10 min. conditioning with 75 g/tonne of R-3501 (isoamyldithiophosphate) at the specified flotation pH. In subsequent tests, the residue was slurried to 30% solids and preleached at pH 1.0 or 3.0 and 20°C or 70°C for 1 h prior to filtration, washing and subsequent conditioning with sulphide and reagent as described above.

A final series of tests was then conducted with residue from both Ponds I and II to examine the possibility of obtaining high grade concentrates by two stages of cleaning.

3.3 Results and Discussion

3.3.1 Flotation Rate Studies

The flotation rate studies (Figures 7 and 8) show that the silver selectivity during roughing was very poor, and even acid pretreatment at pH 1.0 (H_2SO_4 consumption of 85 kg/t residue) and 70°C was not able to improve the silver floatability.

3.3.2 Cleaning Tests

Twice-cleaned concentrates, assaying 0.1-0.2% Ag and 22-35% Zn, were obtained at <16% silver recovery (Tables IV to VI). Conditioning with acid or sulphide prior to flotation had no significant effect on cleaner concentrate grade or recovery.

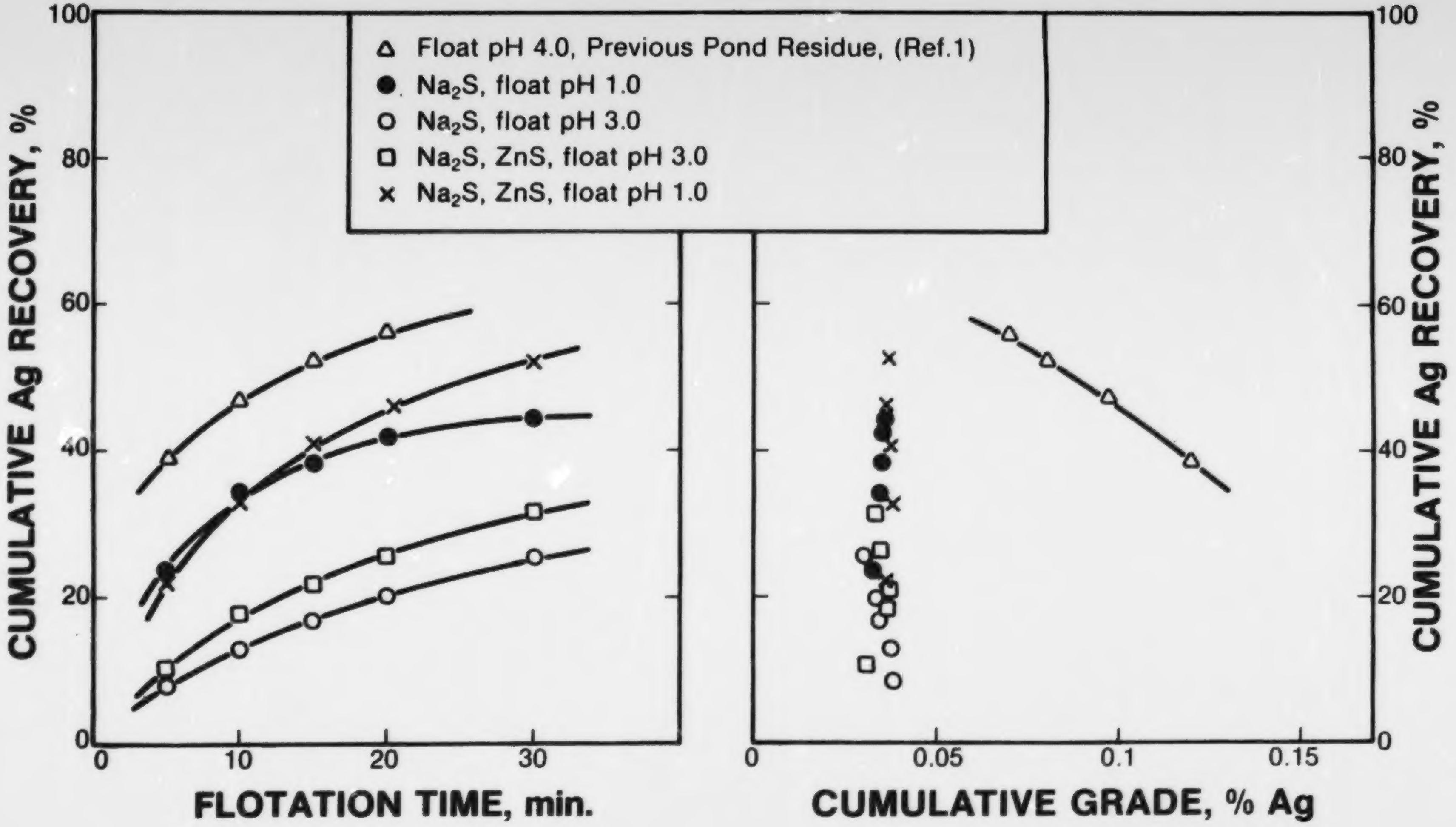

Figure 7. Flotation rate and grade-recovery relationship during rougher flotation of CEZ Pond I residue (All residue samples were conditioned at flotation pH for 10 min. at 20°C prior to sulphide and reagent conditioning).

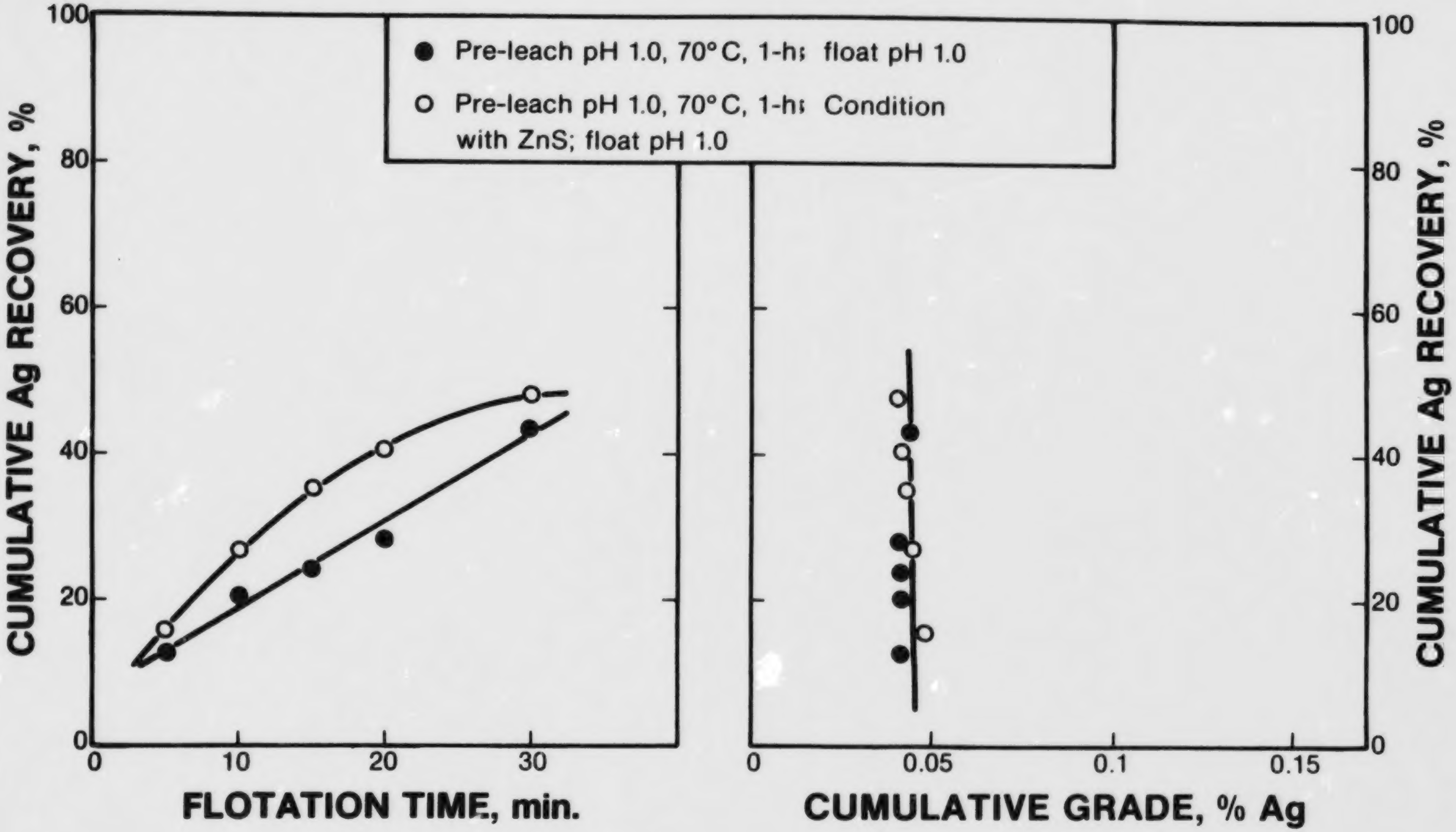

Figure 8. Flotation rate and grade-recovery relationship during rougher flotation of CEZ Pond I residue that had been preleached for 1 h at pH 1.0 and 70°C.

TABLE IV

FLOTATION OF POND I RESIDUE

Fractions	Wt.%	Assay, %		Distribution,%	
		Ag	Zn	Ag	Zn
T-51 Sulphidization. pH 3.0					
Cl. Conc.	1.08	0.193	31.3	9.6	1.7
Cl. 2 Tail	1.66	0.027	20.1	2.1	1.7
Cl. 1 Tail	12.42	0.022	19.7	12.8	12.7
Rgh. Tail	84.84	0.019	19.1	75.5	83.9
Heads	100.00	0.021	19.3	100.0	100.0
T-65 Sulphidization. pH 4.5					
Cl. Conc.	0.91	0.14	29.0	5.1	1.4
Cl. 2 Tail	1.74	0.029	20.1	2.0	1.8
Cl. 1 Tail	10.70	0.032	18.9	13.6	10.6
Rgh. Tail	86.65	0.023	18.9	79.3	86.2
Heads	100.00	0.025	19.0	100.0	100.0
T-66 No Sulphidization. pH 3.0					
Cl. Conc	0.93	0.203	34.5	8.0	1.6
Cl. 2 Tail	2.36	0.035	20.0	3.5	2.4
Cl. 1 Tail	12.05	0.024	20.1	12.4	12.3
Rgh. Tail	84.66	0.021	19.5	76.1	83.7
Heads	100.00	0.023	19.7	100.0	100.0
T-68 No Sulphidization. pH 4.5					
Cl. Conc.	1.04	0.107	28.9	5.0	1.5
Cl. 2 Tail	1.54	0.033	20.7	2.2	1.6
Cl. 1 Tail	14.85	0.023	20.3	15.3	15.2
Rgh. Tail	82.57	0.021	19.6	77.5	81.7
Heads	100.00	0.022	19.8	100.0	100.0

TABLE V

FLOTATION OF POND I RESIDUE

Fractions	Wt.%	Assay, %		Distribution,%	
		Ag	Zn	Ag	Zn
T-47 Pre-treatment at pH 1.0 and 20°C 1-h floated with sulphidization. pH 3.0					
Cl. Conc.	1.52	0.134	23.5	9.0	1.9
Cl. 2 Tail	3.10	0.031	15.8	4.2	2.7
Cl. 1 Tail	14.26	0.027	17.0	17.0	13.2
Rgh. Tail	81.12	0.019	18.5	67.8	88.2
Heads	**100.00**	0.023	18.3	**100.0**	**100.0**
T-48 Pre-treatment at pH 1.0 and 70°C 1-h floated with sulphidization. pH 3.0					
Cl. Conc.	1.74	0.142	24.0	10.9	2.2
Cl. 2 Tail	3.07	0.030	18.0	4.1	2.9
Cl. 1 Tail	15.56	0.024	19.1	16.5	15.9
Rgh. Tail	79.63	0.019	18.6	68.5	79.0
Heads	**100.00**	0.023	18.7	**100.0**	**100.0**
T-49 Pre-treatment at pH 3.0 and 20°C 1-h floated with sulphidization. pH 3.0					
Cl. Conc	1.02	0.131	26.1	6.0	1.4
Cl. 2 Tail	1.87	0.031	17.2	2.6	1.7
Cl. 1 Tail	10.78	0.020	17.1	9.7	9.9
Rgh. Tail	86.33	0.021	18.8	81.7	87.0
Heads	**100.00**	0.022	18.7	**100.0**	**100.0**
T-50 Pre-treatment at pH 3.0 and 70°C 1-h floated with sulphidization. pH 3.0					
Cl. Conc.	0.95	0.155	28.2	6.6	1.4
Cl. 2 Tail	2.48	0.024	17.5	2.7	2.4
Cl. 1 Tail	11.96	0.021	17.4	10.8	11.4
Rgh. Tail	84.61	0.021	18.3	79.9	84.8
Heads	**100.00**	0.022	18.3	**100.0**	**100.0**

TABLE VI

FLOTATION OF POND II RESIDUE

Fractions	**Wt.%**	**Assay, %**		**Distribution,%**	
		Ag	**Zn**	**Ag**	**Zn**
T-52 No Pre-treatment. Sulphidization. pH 3.0					
Cl. Conc.	1.70	0.152	30.0	15.7	3.5
Cl. 2 Tail	0.70	0.041	11.9	1.7	0.6
Cl. 1 Tail	7.63	0.023	11.0	10.8	5.7
Rgh. Tail	89.97	0.013	14.7	71.8	90.2
Heads	**100.00**	0.016	14.7	**100.0**	**100.0**
T-53 Pre-treatment, pH 1.0, 20°C 1-h Sulphidization, pH 3.0					
Cl. Conc.	2.95	0.097	22.2	16.0	4.8
Cl. 2 Tail	1.88	0.027	8.63	2.8	1.2
Cl. 1 Tail	12.26	0.021	10.6	14.4	9.8
Rgh. Tail	82.91	0.014	13.9	66.8	84.4
Heads	**100.00**	0.018	13.6	**100.0**	**100.0**
T-54 Pre-treatment, pH 1.0, 70°C 1-h Sulphidization, pH 3.0					
Cl. Conc	2.67	0.081	24.4	12.7	4.8
Cl. 2 Tail	1.09	0.024	9.16	2.4	1.2
Cl. 1 Tail	14.89	0.021	10.4	18.5	11.4
Rgh. Tail	80.75	0.014	13.8	62.4	82.0
Heads	**100.00**	0.017	13.6	**100.0**	**100.0**
T-130 No Pre-treatment. No Sulphidization, pH 3.0 (average of 2 tests)					
Cl. Conc.	2.27	0.126	28.5	15.8	4.3
Cl. 2 Tail	3.40	0.025	12.7	4.7	2.9
Cl. 1 Tail	16.44	0.017	12.9	15.4	14.1
Rgh. Tail	77.89	0.015	15.2	64.1	78.7
Heads	**100.00**	0.018	15.0	**100.0**	**100.0**

3.4 Conclusions

The silver contained in the residue ponds is not amenable to recovery by conventional flotation procedures, and mild acid treatment prior to flotation is not effective in cleaning surfaces and/or liberating silver in a floatable form.

The reasons for the overall poor silver recoveries and the variability in flotation response between the current samples and those examined previously cannot be readily defined. The physical and chemical characteristics of the CEZ pond residues are known to be highly variable, as these residues were produced and impounded over a number of years, during which time the leach process evolved and concentrates from four mines were treated. Ageing of these residues over the years may also be a factor.

4. LEACH RESIDUE FLOTATION

CEZ operates(4) the jarosite conversion process in which calcine is sequentially subjected to (i) neutral leaching for solubilization of zinc oxide and precipitation of any solubilized iron as ferric hydroxide, (ii) low acid leaching (LAL) for the solubilization of any remaining zinc oxide and generation of a ferrite residue, and (iii) the conversion stage for the simultaneous dissolution of zinc ferrite and precipitation of jarosite. The process provides excellent zinc extractions, but does not yield an enriched silver residue, comparable to a high acid leach residue, that is amenable to further processing for silver recovery.

The feasibility of recovering silver from conversion process residues was investigated in a phased approach. Initial residue samples were taken from the CEZ leach circuit in October 1985 and subjected to silver flotation under standard conditions. Subsequently, a leach pilot plant was established at CEZ to generate process residues under closely controlled conditions and to produce residue from a variety of calcine samples.

4.1 CEZ Circuit Samples

4.1.1 Samples and Procedure

Residue samples were taken from tanks 1 and 3 of the neutral leach, the LAL tank and the LAL thickener underflow (Figure 9). Jarosite samples were not taken from the conversion circuit as previous work(1) had shown that silver-bearing jarosite is not amenable to recovery by flotation. All samples were filtered and washed thoroughly.

The samples (Table VII) contain significant amounts of jarosite, and this is to be expected given the conditions in tank 1 of the neutral leach and the LAL, in addition to the extensive recycle of solution and solids from the conversion circuit and the LAL circuit thickener overflows. The high zinc content of the solids from tank 3 of the neutral leach is

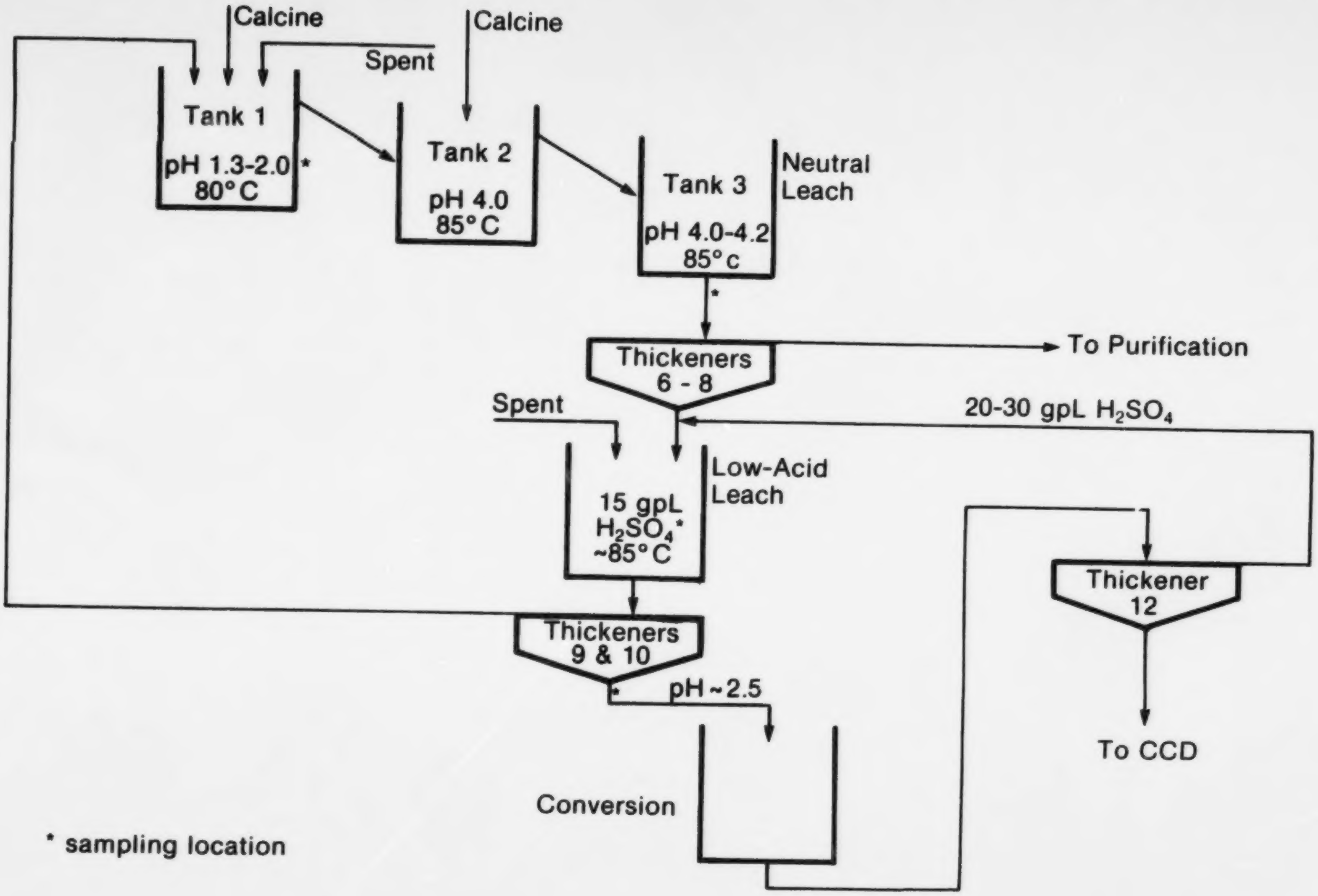
Calcine
Spent
Calcine
Tank 1
pH 1.3-2.0 *
80° C
Tank 2
pH 4.0
85° C
Tank 3
pH 4.0-4.2
85° c
Neutral Leach
*
Thickeners 6 - 8
To Purification
Spent
20-30 gpL H_2SO_4
Low-Acid Leach
15 gpL H_2SO_4 *
~85° C
Thickener 12
Thickeners 9 & 10
*
pH ~ 2.5
To CCD
Conversion
* sampling location

Figure 9. Schematic of CEZ flowsheet showing location of residue sample points(*).

due to the presence of excess zinc oxide. All residue samples were minus 200 mesh, except for the tank 3 neutral leach residue which was 75% minus 200 mesh.

TABLE VII

ANALYSIS OF CEZ CIRCUIT SAMPLES

SAMPLES	Assays, %					
	Ag	Zn	Fe	Pb	$S^=$	$S(SO_4^=)$
NL I tank 1	0.037	16.7	27.1	-	0.91	4.56
NL I tank 3	0.008	39.9	11.7	0.4	0.37	4.12
LAL tank	0.034	18.9	36.2	1.93	1.02	2.83
Thickener 9 U/F	0.018	11.5	33.9	2.20	1.14	8.78

For flotation, the washed residue samples, as received, were slurried at about 30% solids and the pulp pH was adjusted to pH 3.0-3.5 (natural pH was 3.5-4.1) with sulphuric acid. Conditioning with 100 g/t $Na_2S \cdot 9H_2O$ was done for 10 min. A further 10-min. conditioning was done with the addition of 130 g/t R-3501 (Dithiophosphate : American Cyanamid Co.). Rougher flotation was then performed for 25 min. with Aerofroth 65 (American Cyanamid Co.) as required. The rougher concentrate was cleaned once or twice, depending on the sample, at the designated pH to collect the final silver concentrate. Since the objective was to examine the flotation response, the flotation conditions were not varied during these tests and the applied flotation conditions may not have been optimum for a particular sample.

4.1.2 Results and Discussion

The silver distribution to the various flotation products and the grade-recovery relationships in roughing and cleaning are given in Table VIII and Figure 10, respectively.

TABLE VIII

RESULTS OF SILVER FLOTATION WITH CEZ CIRCUIT SAMPLES

Fractions	Wt.%	Assay, %		Distribution,%	
		Ag	Zn	Ag	Zn
NEUTRAL LEACH TANK 1					
Conc.	4.46	0.545	54.1	61.8	14.8
Cl. 2 Tail	1.78	0.081	16.3	3.7	1.8
Cl. 1 Tail	16.50	0.027	16.3	11.3	16.5
Rgh. Tail	77.26	0.012	14.1	23.2	66.9
Heads	100.00	0.0393	16.3	100.0	100.0
NEUTRAL LEACH TANK 3					
Conc.	0.91	0.10	39.9	11.7	0.9
Cl. 1 Tail	3.78	0.028	15.4	13.6	1.5
Rgh. Tail	95.31	0.0061	39.0	74.7	97.6
Heads	100.00	0.0078	38.1	100.0	100.0
LOW ACID LEACH TANK					
Conc.	2.01	0.712	46.4	43.4	5.0
Cl. 2 Tail	0.58	0.181	17.5	3.3	0.5
Cl. 1 Tail	7.88	0.055	18.4	13.5	7.7
Rgh. Tail	89.53	0.014	18.2	39.8	86.8
Heads	100.00	0.0321	18.8	100.0	100.0
THICKENER NO. 9 U/F					
Conc.	3.10	0.209	18.5	21.8	6.9
Cl. 2 Tail	2.41	0.038	8.30	3.1	2.4
Cl. 1 Tail	14.55	0.024	7.84	11.8	13.8
Rgh. Tail	79.94	0.024	7.96	63.3	76.9
Heads	100.00	0.0297	8.28	100.0	100.0

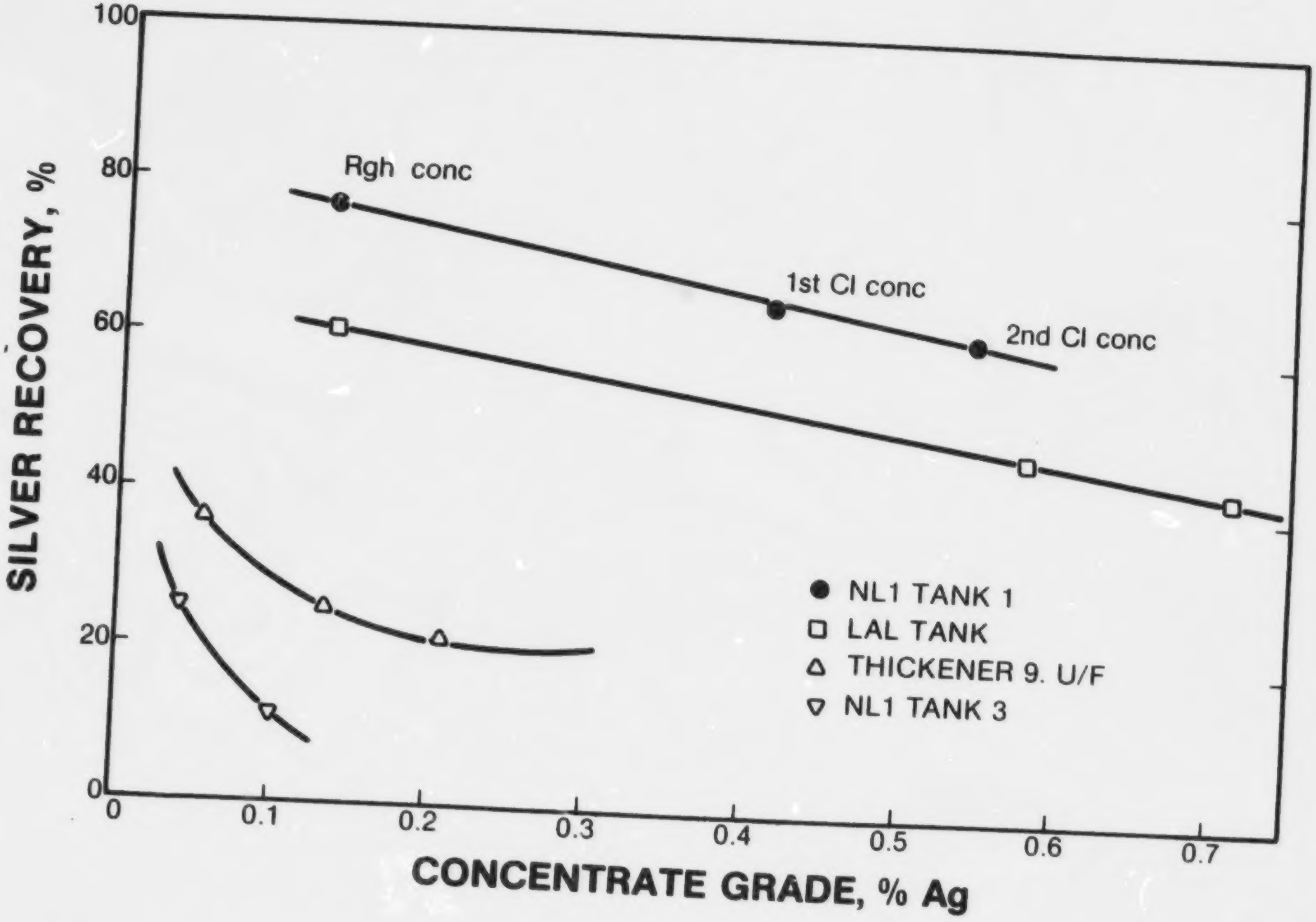

Figure 10. Grade-recovery relationship in roughing and cleaning of CEZ circuit samples.

The best results were obtained with residue from neutral leach tank 1 which gave a rougher concentrate assaying 0.13% Ag with 76.8% silver recovery. After two cleanings a silver concentrate containing 0.545% Ag was obtained with 61.8% recovery. The neutral leach tank 3 sample showed extremely poor silver flotation. This is attributed to the precipitation of iron, dissolved in tank 1, during progression of the pulp through tanks 2 and 3 of the neutral leach that fouls the silver mineral surfaces. The effect of precipitated iron on silver flotation will be discussed later (Section 4.3).

The residue sample taken from the low acid leach tank gave a twice-cleaned silver concentrate assaying 0.712% Ag with 43.4% recovery. The rougher concentrate contained 60.2% of the silver in the feed at a grade of 0.135% Ag. The improved silver recovery from this residue compared to that of neutral leach tank 3 residue is believed to be due to dissolution of metal hydroxides which precipitated during the last stages of the neutral leach. However, the silver recovery was not restored to the value obtained with the neutral leach tank 1 residue, and it appears that neutralization of the residue slurry to pH 3-4 reduces silver recovery by about 20% even if the residue is reacidified to pH 1.5. The relatively low sulphate level of the sample indicates that there were no jarosite solids in the thickener 12 O/F returned to the LAL at the time of sampling.

The rougher concentrate produced from LAL thickener underflow assayed only 0.05% Ag and contained 36.7% of the silver in the feed. A twice-cleaned concentrate assaying 0.21% Ag was obtained with only 21.8% silver recovery. The poor silver floatability is attributed to (i) the relatively short (<20 min.) retention time in the LAL tank, with resultant continuing reactions in the thickener and precipitation of iron hydroxide due to the acid consumption, and (ii) a significant amount of jarosite in the thickener underflow residue.

It is evident from the above results that the silver floatability is highly dependent upon the leach conditions in each stage and that a thorough understanding of the effect of leach conditions on flotation is required.

4.2 Pilot Plant Residues

To investigate the effects of leach conditions, residue flocculation, residue washing, metal content of the flotation media, and calcine source on silver floatability and recovery, a leach pilot plant was assembled at CEZ to generate representative samples of residue for use in batch and locked cycle flotation studies. Leaching in the pilot plant was conducted in both batch and continuous modes, depending upon the leach stage and the amount of calcine available.

4.2.1 Residue Generation

A description of the equipment and leach procedures employed to generate neutral leach tank 1, neutral leach tank 3, low acid leach and high acid leach (HAL) residues is given in Appendix I. Five calcine samples (Table IX) were employed, and most of the emphasis was placed on generation and flotation of neutral leach tank 1 residue. Specific neutral leach parameters investigated, in addition to the source of calcine, were the pH in the neutral leach tank 1, the recycle of LAL thickener O/F to tank 1 and the addition of zinc concentrate to tank 1 as a silver collector. The LAL and the HAL residues were produced under fixed conditions, as the objective of these tests was primarily to determine if any loss in silver floatability during neutral leaching could be restored by subsequent acidic leach steps.

TABLE IX

ANALYSIS OF CALCINE SAMPLES

CALCINE[1]	Analysis, %						
	Zn	Fe	Pb	Ag	S_T	$S(SO_4)$	$S^=$
CEZ I	59.4	9.89	2.00	0.012	4.5	4.2	0.3
CEZ II	61.1	12.0	2.41	0.010	2.98	2.59	0.39
Kidd Creek	61.8	11.6	0.94	0.013	2.19	1.92	0.27
A	58.7	6.67	2.45	0.034	3.48	3.04	0.44
B	65.2	5.28	3.99	0.019	1.30	1.15	0.15

[1] Calcine samples A and B were obtained from zinc plants outside North America.

4.2.2 Flotation of Neutral Leach Residues

4.2.2.1 Neutral Leach Residue from CEZ Calcine

Washed residue samples were slurried at about 30% solids and the pulp pH was adjusted to pH 3-4 (natural pH ranged from 3.5-6.2) with sulphuric acid. When sulphidization was employed, conditioning with 100 g/t $Na_2S{\bullet}9H_2O$ or 3% by weight of Brunswick zinc concentrate was done for 10 min. A further 10-min. conditioning was then given with the addition of 200 g/t R-3501 (dithiophosphate, American Cyanamid Co.) and 200 g/t S-4037 (thionocarbamate). Rougher flotation was performed for 20-30 min. with addition of Aerofrother 65 as required. The rougher concentrate was cleaned once or twice, except in the rate studies where rougher concentrate samples were taken at predetermined time intervals.

The neutral leach and residue flotation conditions employed, the leach residue assays and the flotation results, are given in Tables X and XI, and Figures 11 to 15.

The effects of leach medium and pH on silver recovery, when floating tank 1 residue with sodium sulphide conditioning, are shown in Figure 11. As can be seen, addition of low acid leach overflow with spent electrolyte during calcine leaching adversely affects the silver concentrate grade; pH 1.5 leaching is preferred. Addition of zinc concentrate during calcine leaching, sulphidization of washed leach residue with sodium sulphide, and conditioning of leach residue with ZnS prior to flotation do not appear to have any significant effect on silver recovery (Figures 12 and 13). However, the co-flotation of added zinc sulphide causes a reduction in the silver grade of the flotation concentrate.

The results of rougher and two stages of cleaner flotation, with and without superficial sulphidization with 100 g/t $Na_2S \cdot 9H_2O$, with low acid leach overflow at pH 1.5 gave concentrates containing higher silver contents than those produced from residues generated at pH 3.0. Furthermore, a better silver grade was obtained when the residue was floated without sulphidization, indicating that a portion of the silver in the residue was depressed by Na_2S.

Similar tests, with and without superficial sulphidization, using leach residues obtained by leaching with only spent electrolyte and water at pH 1.5 and 3.0 have shown (Figure 15) that increased silver floatability and selectivity are obtained without sulphidization prior to flotation. Furthermore, the effect is highly pronounced with residues prepared at pH 1.5 without the addition of low acid leach overflow. The silver concentrate produced after one stage of cleaning assayed 2.1% Ag with 82% silver recovery.

The rougher-cleaner flotation tests using residues obtained by leaching calcine in the presence of zinc concentrate (3% by calcine weight) at pH 1.5 and 3.0, with or without low acid leach overflow gave somewhat erratic results. However, no beneficial effect resulted from leaching calcine with added ZnS.

TABLE X

ANALYSIS OF NEUTRAL LEACH RESIDUES PRODUCED FROM CEZ CALCINES

Residue Sample	Analysis, %						
	Zn	Fe	Pb	Ag	S_T	$S(SO_4)$	$S(S^=)$
Residues from CEZ Calcine I							
1	22.8	38.3	8.3	0.043	2.1	1.8	0.3
2	22.0	39.2	8.3	0.044	1.6	1.3	0.3
3	17.3	34.1	4.8	0.027	2.7	2.4	0.3
4	24.0	38.1	7.2	0.030	1.3	1.2	0.1
5	22.0	37.6	9.0	0.032	3.1	1.8	1.3
6	22.5	36.9	9.5	0.045	4.0	1.7	2.3
8	25.2	35.8	6.8	0.041	3.2	1.1	2.1
Residues from CEZ Calcine II							
9	24.9	38.8	9.4	0.042	2.3	1.5	0.8
10	21.0	39.4	-	0.027	2.8	1.5	1.3
11	22.7	25.7	-	0.016	3.5	2.6	0.9
12	23.1	39.0	9.8	0.025	2.9	1.6	1.3

The floatability of silver in tank 3 neutral leach residue, examined in a series of tests conducted with residue produced from CEZ calcine II, was found to be poor (Table XI, tests 147-149). This is expected based upon the results from the flotation of tank 1 neutral leach residue generated at pH 3. The poor flotation is believed to be due to the precipitation of iron and other metals during neutralization of the zinc electrolyte to pH 4.0-4.2 in tank 3.

Two sets of locked cycle tests (5 cycles), using composite samples of neutral leach residue from the CEZ pilot plant, were carried out to examine the flotation response of silver when the cleaner tailings were recycled. In each test, two stages of cleaning were employed and the

TABLE XI

SILVER FLOTATION OF NEUTRAL LEACH RESIDUES PRODUCED FROM CEZ CALCINE

Test No.	Residue	Leach Conditions[1]				Sulphidization		Assay, %						Recovery, %			
		LAL[2] O/F	ZnS[3] add.	pH Tank 1	pH Tank 3	ZnS Addn wt.%	$Na_2S \cdot 9H_2O$ Addition g/tonne	Cleaner 2 Conc. Ag	Cleaner 2 Conc. Zn	Cl.1 Conc. Ag	Rgh Conc. Ag	Rgh Tails Ag	Heads Ag	Cl. 2 Conc. Ag	Cl. 2 Conc. Zn	Cl. 1 Conc. Ag	Rgh Conc. Ag
77	1	Y	N	1.5	-	0	100	-	-	-	0.176	0.018	0.0432	-	-	-	65.0
78		Y	N	1.5	-	3	0	-	-	-	0.136	0.016	0.0430	-	-	-	71.2
79		Y	N	1.5	-	0	100	1.140	27.0	0.821	0.139	0.017	0.043	30.2	1.5	47.9	68.9
90		Y	N	1.5	-	0	0	1.820	33.4	0.92	0.182	0.020	0.0455	26.3	1.0	45.7	63.2
91	2	N	N	1.5	-	0	100	-	-	-	0.178	0.0176	0.0479	-	-	-	70.3
92		N	N	1.5	-	3	0	-	-	-	0.139	0.0163	0.0454	-	-	-	72.5
93		N	N	1.5	-	0	100	-	-	1.92	0.266	0.016	0.0477	-	-	50.8	70.2
124		N	N	1.5	-	0	0	7.20	43.5	2.06	0.231	0.0075	0.0511	65.9	0.9	81.5	88.2
94	3	Y	N	3.0	-	0	100	-	-	-	0.058	0.0116	0.0293	-	-	-	75.6
95		Y	N	3.0	-	0	100	0.531	17.5	0.090	0.051	0.0114	0.0284	57.7	3.3	68.4	77.3
96		Y	N	3.0	-	3	0	-	-	-	0.0511	0.013	0.0295	-	-	-	75.1
117		Y	N	3.0	-	0	100	0.42	14.5	0.106	0.045	0.0136	0.0244	44.4	2.4	50.3	63.5
125		Y	N	3.0	-	0	0	0.836	16.2	0.156	0.051	0.016	0.0285	40.8	1.4	51.7	63.8
97	4	N	N	3.0	-	0	100	-	-	-	0.110	0.0144	0.0428	-	-	-	76.4
98		N	N	3.0	-	0	100	1.49	28.0	0.46	0.125	0.018	0.0445	48.8	1.8	55.5	69.6
99		N	N	3.0	-	3	0	-	-	-	0.119	0.012	0.0437	-	-	-	80.7
118		N	N	3.0	-	0	100	1.49	28.0	0.443	0.116	0.017	0.0402	52.0	1.7	56.8	67.7
126		N	N	3.0	-	0	0	3.07	36.6	0.772	0.152	0.0146	0.0425	58.3	1.3	63.7	72.5
100	5	Y	Y	1.5	-	0	0	-	-	-	0.0528	0.021	0.0345	-	-	-	65.0
102		Y	Y	1.5	-	0	0	0.53	31.3	0.58	0.124	0.010	0.0333	45.4	4.2	61.9	76.1
119		Y	Y	1.5	-	0	0	0.738	34.3	0.474	0.114	0.011	0.0336	54.1	4.0	64.1	74.5
103	6	N	Y	1.5	-	0	0	-	-	-	0.162	0.628	0.0466	-	-	-	55.0
104		N	Y	1.5	-	0	0	0.26	34.9	0.221	0.160	0.0196	0.0442	35.6	9.8	44.9	63.4
120		N	Y	1.5	-	0	0	0.15	30.9	0.172	0.122	0.025	0.0496	23.3	11.3	38.8	62.3
105	8	N	Y	3.0	-	0	0	-	-	-	0.109	0.013	0.0364	-	-	-	72.9
106		N	Y	3.0	-	0	0	0.36	51.7	0.325	0.114	0.014	0.0404	63.0	14.6	64.3	74.3
121		N	Y	3.0	-	0	0	0.364	49.3	0.267	0.101	0.0138	0.0394	63.8	14.6	66.3	75.5
131	9	N	-	1.5	-	0	0	0.84	40.5	0.609	0.180	0.0147	0.0424	49.8	3.9	58.7	71.3
147	10	Y	-	1.5	4.0	0	0	0.42	41.6	0.275	0.095	0.011	0.0274	22.7	2.6	37.6	67.8
148	11	Y	-	3.0	4.0	0	0	0.19	48.7	0.132	0.045	0.011	0.0173	27.6	5.2	33.4	48.1
149	11	Y	-	3.0	4.0	0	0	0.22	42.0	0.141	0.055	0.011	0.0199	35.9	6.6	42.4	56.0

[1] Detailed leach conditions and procedures are given in Appendix I.

[2] Low acid leach overflow added to tank 1. Y = Yes, N = No.

[3] Brunswick zinc concentrate added to tank 1. Y = Yes, N = No.

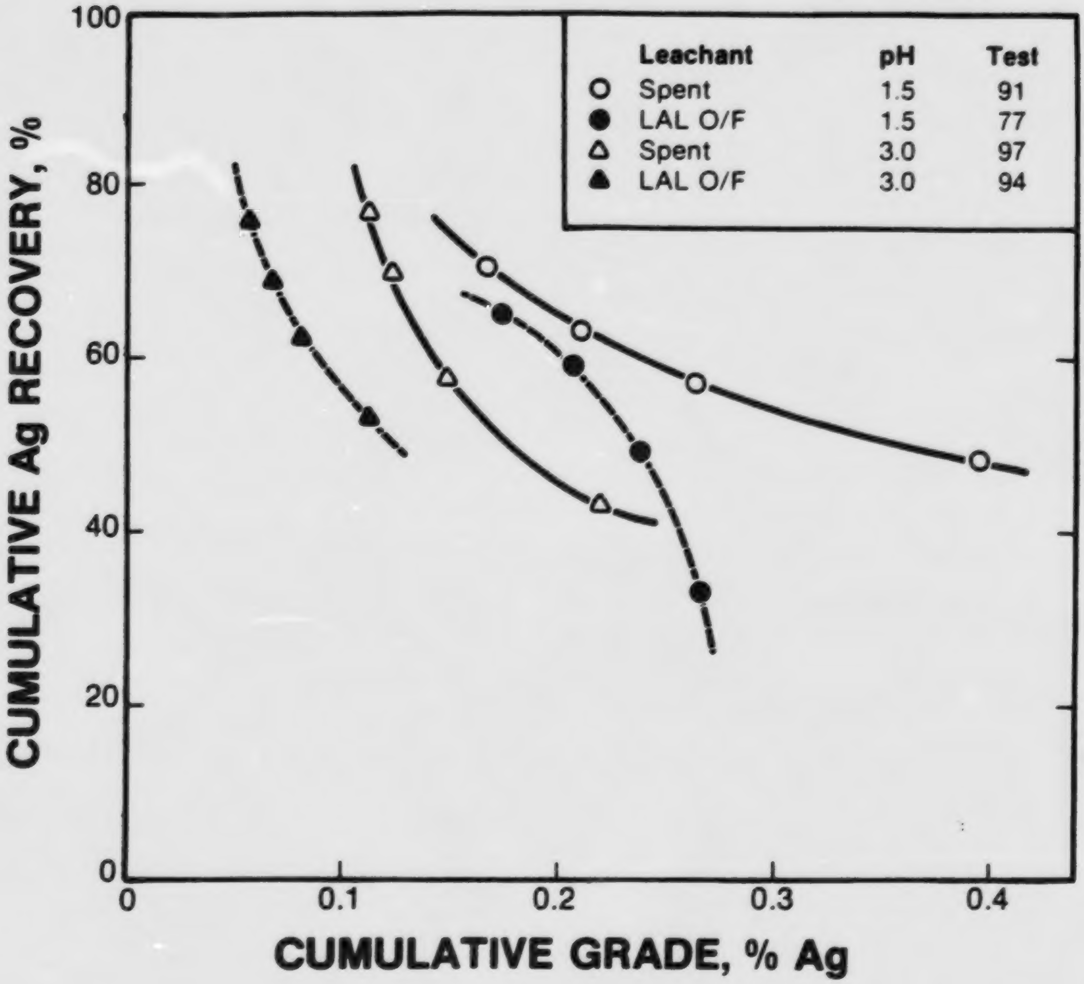

Figure 11. Effect of tank 1 neutral leach pH and leachant on silver recovery and grade during flotation of tank 1 neutral leach residue sulphidized with Na_2S.

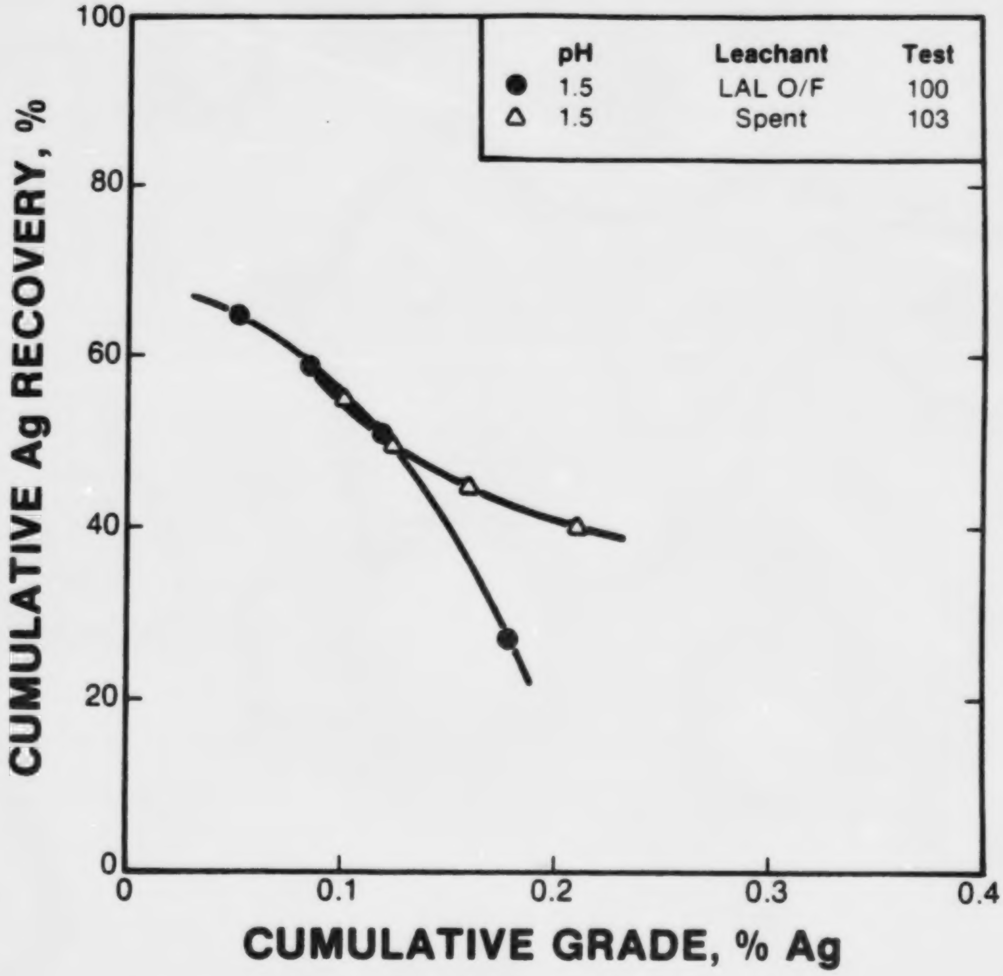

Figure 12. Silver grade and recovery during roughing of tank 1 neutral leach residue produced by leaching in the presence of added zinc concentrate.

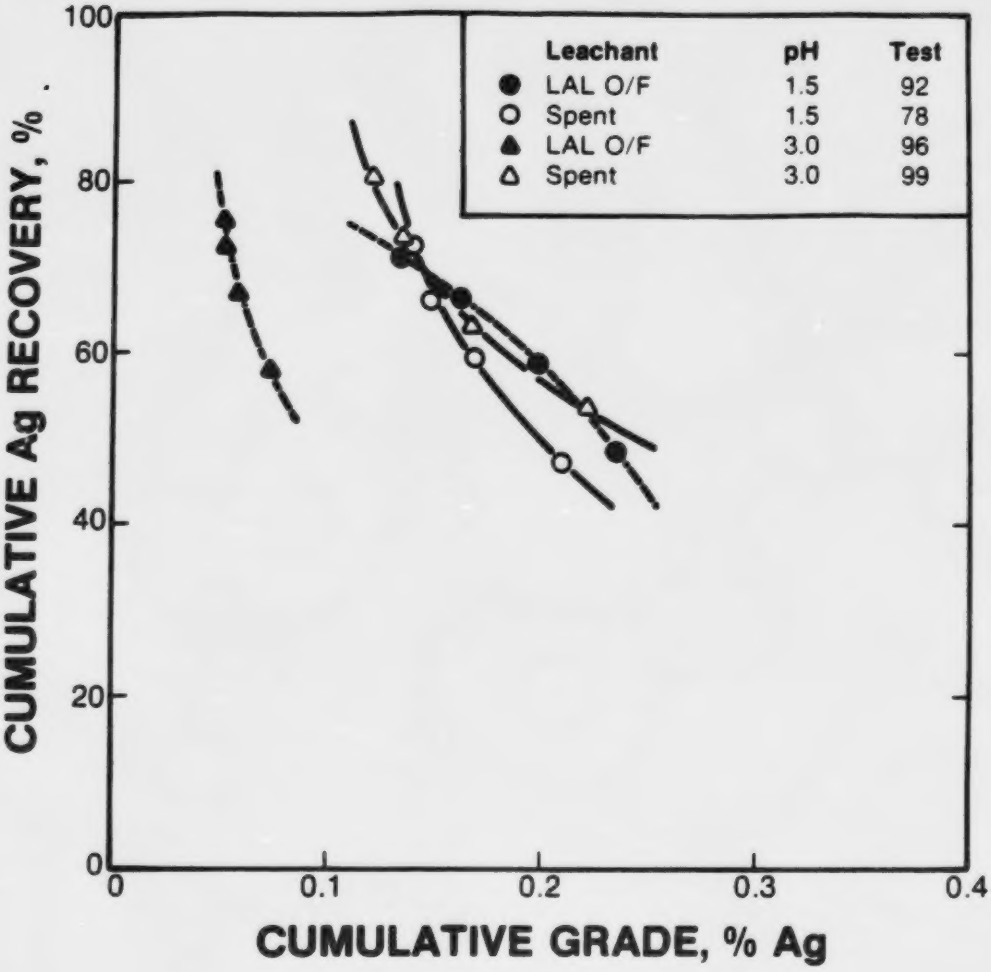

Figure 13. **Silver grade and recovery during roughing of tank 1 neutral leach residue** which was conditioned with zinc concentrate prior to flotation.

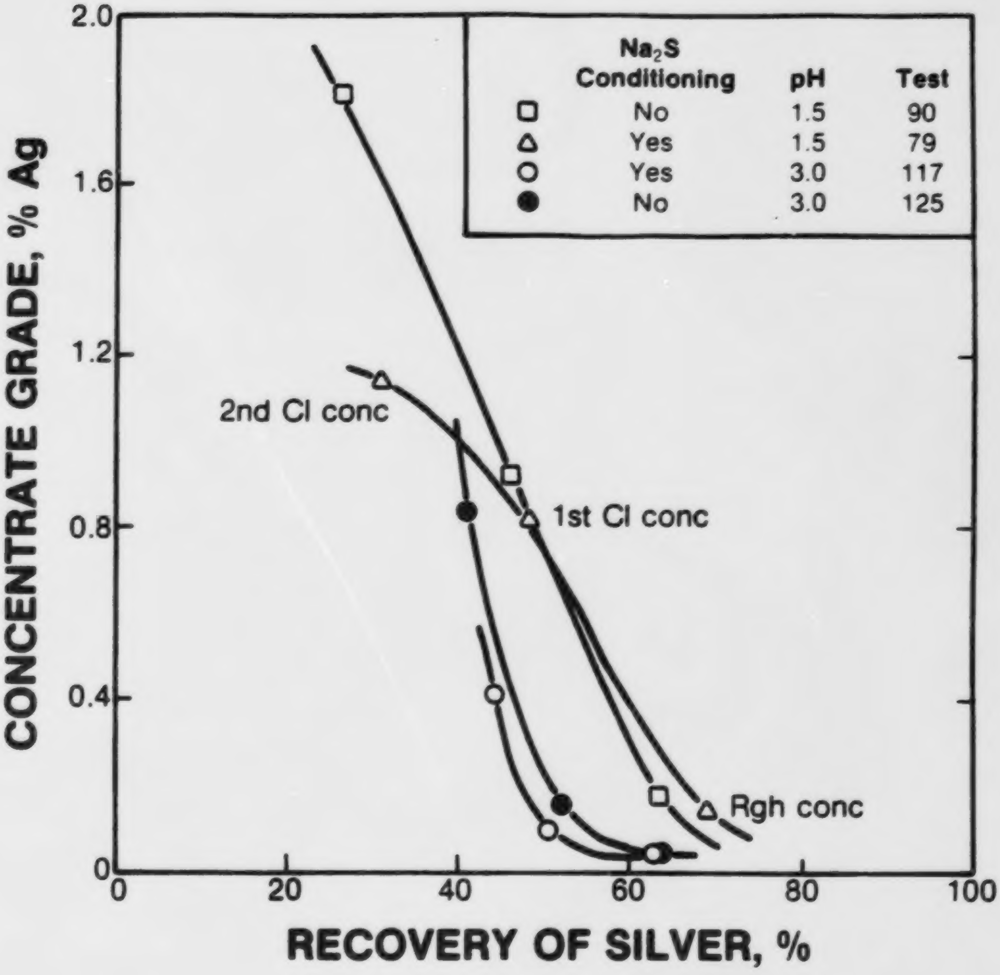

Figure 14. Silver grade and recovery during cleaning of tank 1 neutral leach residue prepared with LAL O/F at pH 1.5 and 3.0 that had been conditioned with and without Na_2S.

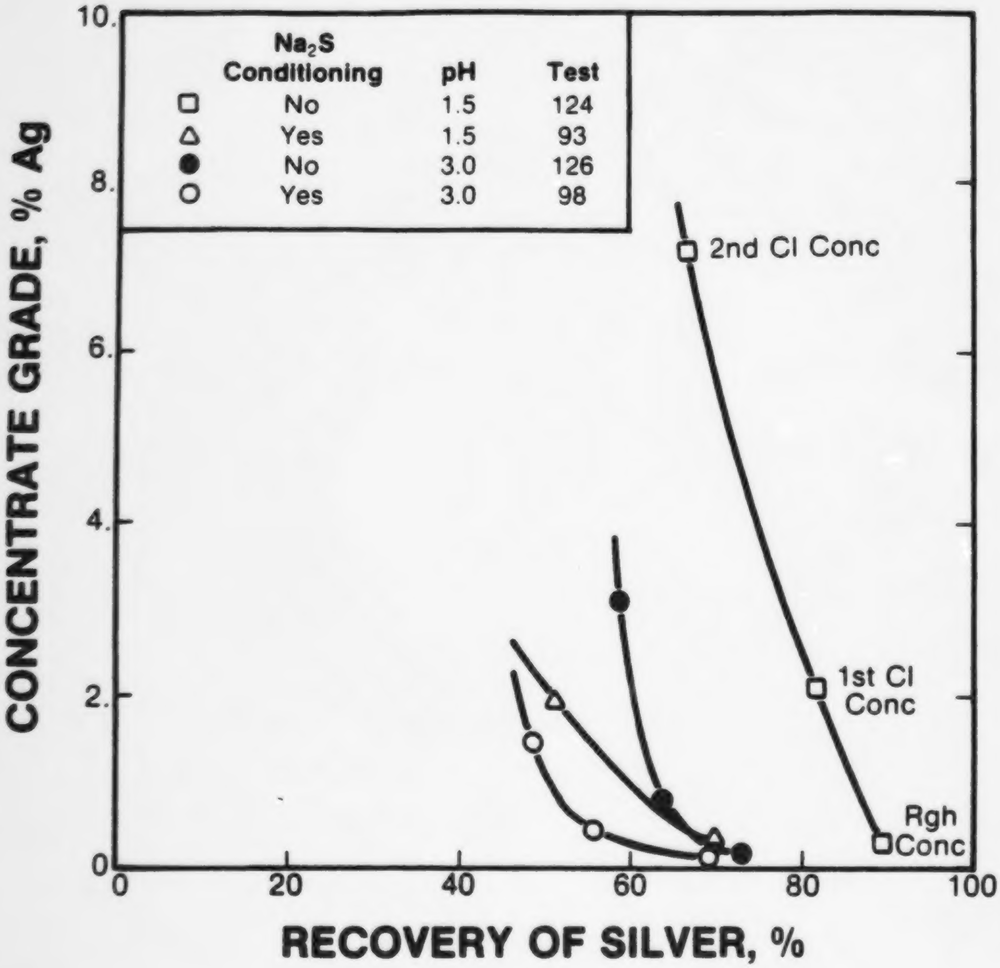

Figure 15. Silver grade and recovery during cleaning of tank 1 neutral leach residue (prepared with spent at pH 1.5 and 3.0) that had been conditioned with and without Na_2S.

TABLE XII

SILVER BALANCE IN LOCKED CYCLE FLOTATION TEST USING COMPOSITE CEZ RESIDUE[1] OBTAINED AT pH 1.5

	Charge		Concentrate			Rougher Tails		Cleaner Tails (calculated)		Recovery,%	
Cycle	wt g	% Ag	wt g	% Ag	% Zn	wt g	% Ag	wt g	% Ag	Ag	Zn
1	1046.0	0.0430	30.3	0.972	41.8	883.2	0.0104	132.5	0.0478	76.6	5.5
2	1048.8	0.0435	31.4	1.066	39.7	992.6	0.0097	155.8	0.0527	78.2	5.8
3	1048.8	0.0442	35.3	1.050	40.6	978.6	0.0098	188.7	0.0345	77.9	7.5
4	1045.0	0.0417	33.4	1.042	40.2	1041.1	0.0092	156.7	0.0444	79.3	7.5
5	1045.5	0.0432	31.3	1.105	41.0	984.7	0.0104	173.7	0.0398	76.5	6.5
Average			-	1.05	40.6	-	0.0099	-	-	77.7	6.6

[1] Residue head assay: 0.043% Ag, 20.8% Zn, 10.2% Pb.

TABLE XIII

SILVER BALANCE IN LOCKED CYCLE FLOTATION TEST USING COMPOSITE CEZ RESIDUE[1] OBTAINED AT pH 3.0

	Charge		Concentrate			Rougher Tails		Cleaner Tails (calculated)		Recovery,%	
Cycle	wt g	% Ag	wt g	% Ag	% Zn	wt g	% Ag	wt g	% Ag	Ag	Zn
1	756.9	0.0358	23.4	0.781	49.6	539.6	0.0109	193.9	0.0151	70.5	9.7
2	758.8	0.0316	25.0	0.755	48.3	647.9	0.0104	277.5	0.0159	71.9	12.2
3	758.2	0.0305	26.4	0.742	50.5	852.0	0.010	153.8	0.0219	73.1	7.3
4	757.9	0.0335	24.6	0.793	51.3	707.7	0.011	177.4	0.0179	70.2	4.2
5	758.0	0.0324	24.6	0.805	49.4	712.0	0.0105	196.6	0.0150	71.6	6.7
Average			-	0.79	49.8	-	0.0105	-	-	71.6	8.0

[1] Residue head assay: 0.035% Ag, 21.0% Zn, 7.0% Pb.

cleaner tailings were recycled without filtration to the head of the next cycle. No sulphidization was employed prior to flotation. The first composite sample comprised all individual residues prepared at pH 1.5, including leaches with low acid leach overflow recycle and zinc sulphide addition. The second sample was a composite of all leach residues produced at pH 3.0.

The residue prepared from calcine leached at pH 1.5 gave an average silver recovery of 77.7% at a concentrate grade of 1.05% Ag. The composite residue from calcine leached at pH 3.0 resulted in a silver concentrate assaying 0.79% Ag at a recovery of 71.6% (Tables XII and XIII). The flotation system was very stable, giving consistent products in each cycle.

4.2.2.2 Neutral Leach Residue from Kidd Creek Calcine

The neutral leach and residue flotation conditions employed, the leach residue assays and the flotation results are given in Tables XIV and XV, and Figures 16 to 18.

TABLE XIV

ANALYSIS OF NEUTRAL LEACH RESIDUES PRODUCED FROM KIDD CREEK CALCINE

Residue Sample	Analysis, %						
	Zn	Fe	Pb	Ag	S_T	$S(SO_4)$	$S(S^{=})$
13	24.0	42.2	3.6	0.049	1.2	0.6	0.6
14	24.2	40.0	3.9	0.056	3.5	0.7	2.8
15	23.8	42.5	3.3	0.038	1.2	0.6	0.6
16	23.7	40.3	3.4	0.040	3.2	0.9	2.3

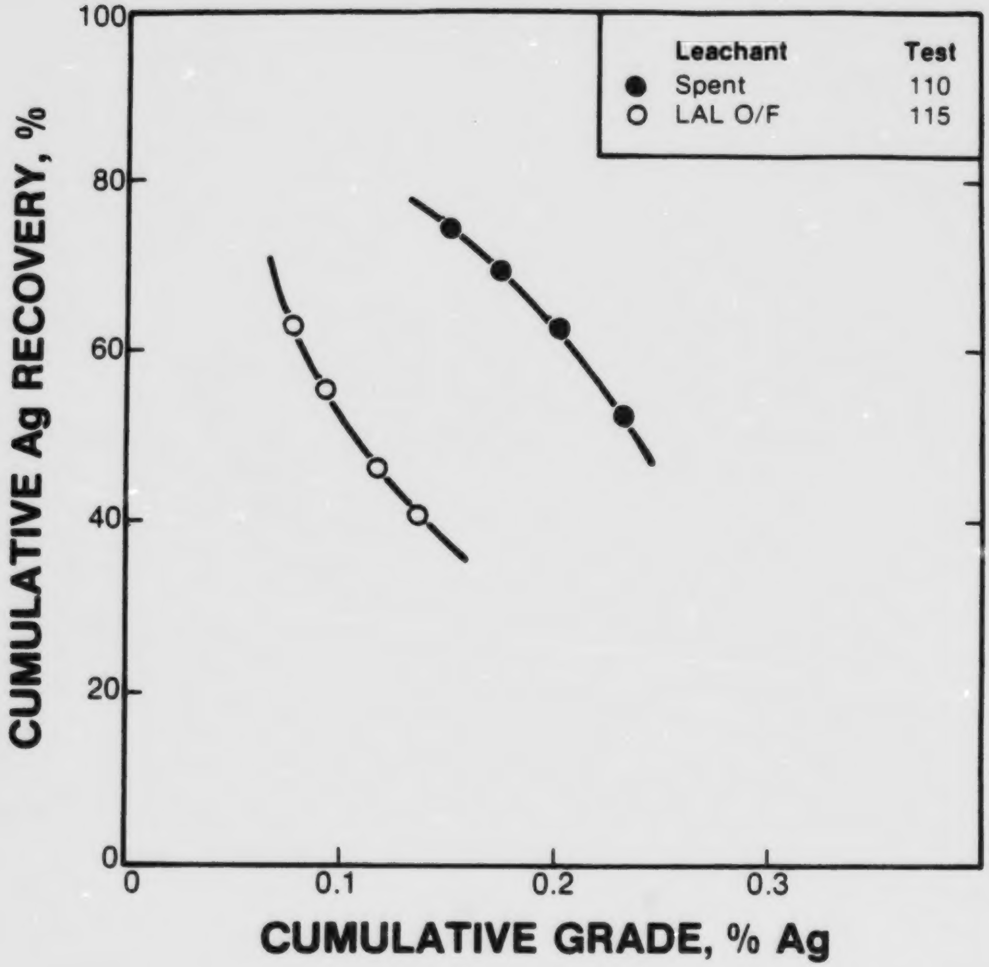

Figure 16. Silver grade and recovery during roughing of tank 1 neutral leach residue produced by leaching KCM calcine at pH 1.5 in the presence of added zinc concentrate.

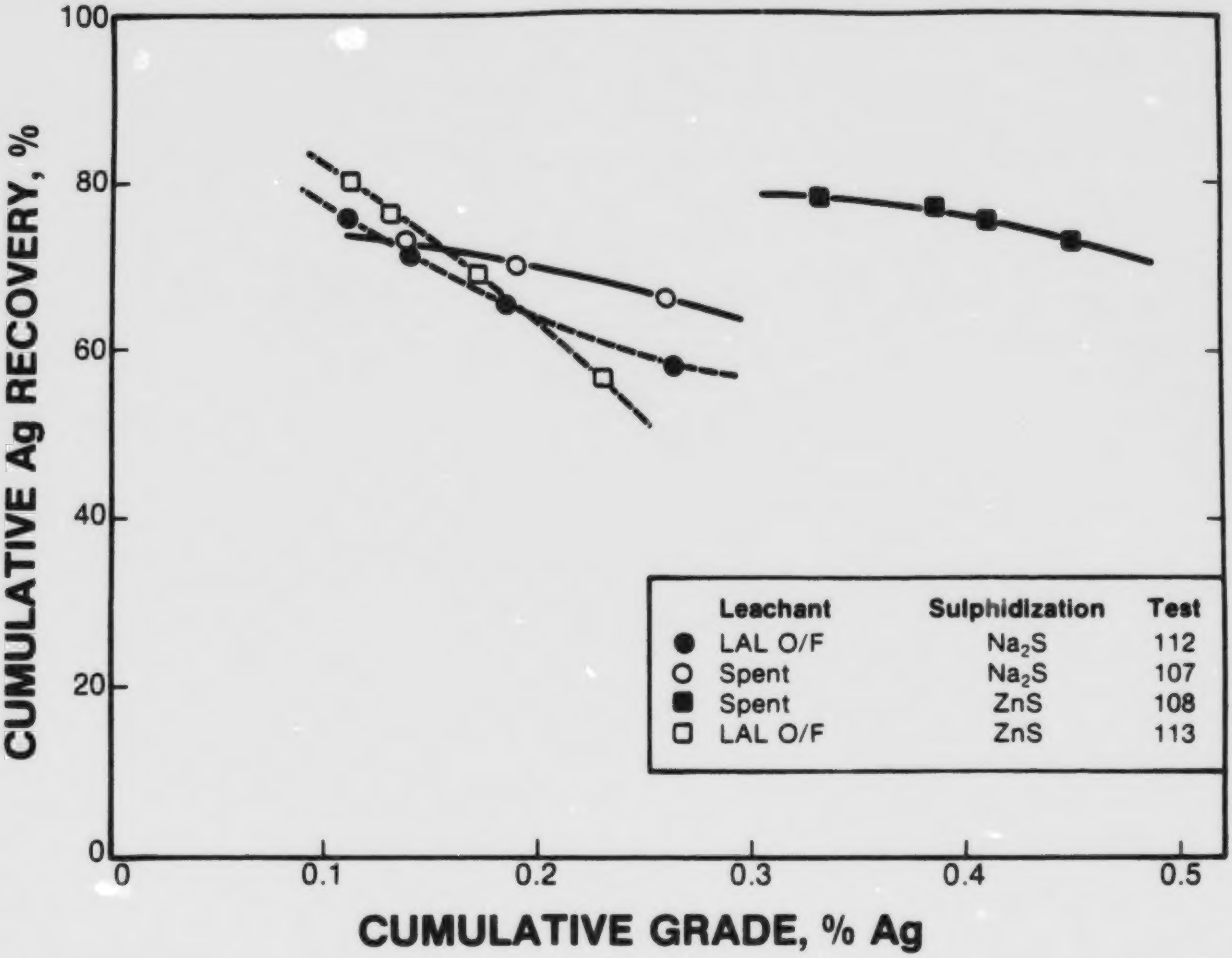

Figure 17. Silver grade and recovery relationship during roughing of tank 1 neutral leach residue that was conditioned with zinc concentrate or sodium sulphide prior to flotation (all residues produced by leaching KCM calcine at pH 1.5).

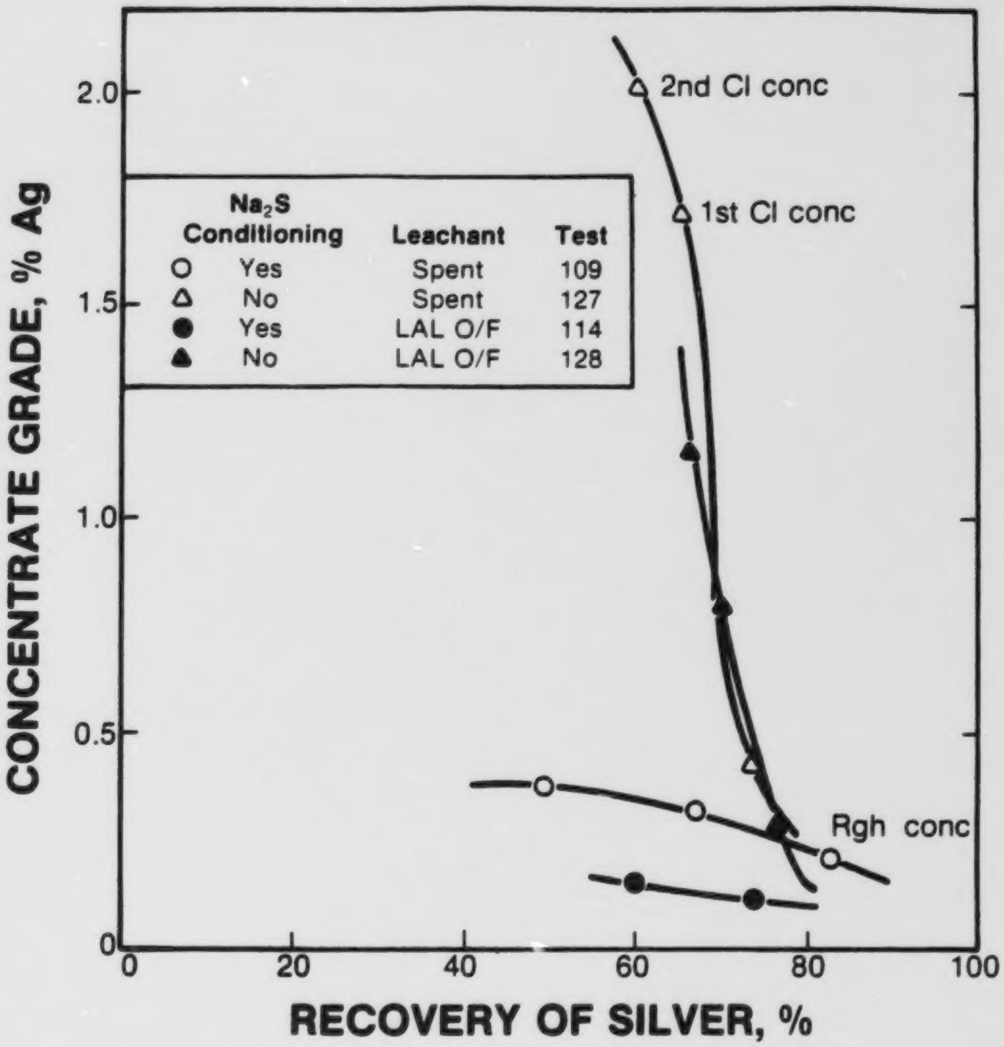

Figure 18. Silver grade and recovery during cleaning of tank 1 neutral leach residue prepared from Kidd Creek calcine at pH 1.5 that had been conditioned with and without Na_2S.

TABLE XV

SILVER FLOTATION OF NEUTRAL LEACH RESIDUES PRODUCED FROM KIDD CREEK CALCINE

Test No.	Residue	Leach Conditions[1]				Sulphidization		Assay, %						Recovery, %			
		LAL[2] O/F	ZnS[3] Added	pH Tank 1	pH Tank 3	ZnS Added %	$Na_2S \cdot 9H_2O$ g/tonne	Cl.2 Conc. Ag	Cl.2 Conc. Zn	Cl.1 Conc. Ag	Rougher Conc. Ag	Rougher Tail Ag	Heads Ag	Cl.2 Conc. Ag	Cl.2 Conc. Zn	Cl.1 Conc. Ag	Rougher Conc. Ag
107	13	N	N	1.5	-	0	100	-	-	-	0.138	0.012	0.0357	-	-	-	72.7
108		N	N	1.5	-	3	0	-	-	-	0.337	0.011	0.0448	-	-	-	78.0
109		N	N	1.5	-	0	100	0.383	31.3	0.334	0.209	0.011	0.0516	49.5	8.6	67.0	83.0
127		N	N	1.5	-	0	0	2.02	55.3	1.734	0.425	0.013	0.0483	60.6	3.3	65.5	75.1
110	14	N	Y	1.5	-	0	0	-	-	-	0.151	0.019	0.0547	-	-	-	74.1
111		N	Y	1.5	-	0	0	0.309	39.3	0.293	0.217	0.020	0.0558	45.9	13.5	50.3	70.7
122		N	Y	1.5	-	0	0	0.468	41.6	0.456	0.204	0.016	0.0524	60.9	12.0	64.6	74.3
112	15	Y	N	1.5	-	0	100	-	-	-	0.110	0.012	0.0373	-	-	-	75.7
113		Y	N	1.5	-	3	0	-	-	-	0.111	0.011	0.0384	-	-	-	80.1
114		Y	N	1.5	-	0	100	-	-	0.148	0.118	0.011	0.0371	-	-	59.8	77.6
128		Y	N	1.5	-	0	0	1.163	42.4	0.796	0.281	0.010	0.0372	66.8	3.9	70.5	76.3
115	16	Y	Y	1.5	-	0	0	-	-	-	0.078	0.019	0.037	-	-	-	63.6
116		Y	Y	1.5	-	0	0	0.227	34.3	0.214	0.159	0.011	0.0388	39.4	10.0	67.0	78.5
123		Y	Y	1.5	-	0	0	0.456	37.5	0.435	0.155	0.010	0.0400	59.4	8.7	72.3	80.0

[1] Detailed leach conditions and procedures are given in Appendix I.

[2] Low acid leach overflow added to tank 1. Y = Yes, N = No.

[3] Brunswick zinc concentrate added to tank 1. Y = Yes, N = No.

Similar to the results obtained with residues from CEZ calcine, leaching the KCM calcine in the presence of ZnS, with LAL O/F, gave poor silver grades and recoveries in flotation when compared to leaching with spent electrolyte (Figure 16). No benefit was obtained by using superficial sulphidization on residues produced either with LAL O/F or spent. However, a test with ZnS conditioning prior to flotation, using residues produced with spent electrolyte, resulted in a higher grade rougher concentrate than for residues produced with LAL O/F (Figure 17).

The results of the roughing-cleaning tests, with and without superficial sulphidization, are shown in Figure 18. Although about 80% of the silver was recovered in roughing in all tests, the silver selectivity during cleaning was highly pronounced when no sulphidization was employed. The silver concentrate obtained from residue produced by leaching at pH 1.5 with spent electrolyte assayed 2.02% Ag, with 61% silver recovery.

A locked cycle (5 cycles) flotation test was conducted using a composite sample of all the leach residues (Table XV) produced from Kidd Creek calcine. The twice-cleaned silver concentrate assayed an average of 0.938% Ag at 81.6% recovery, and the corresponding tails assayed 0.0092% Ag (Table XVI). The flotation system was stable, giving consistent products each cycle.

4.2.2.3 Neutral Leach Residues from Overseas Calcines

Flotation tests were performed with NL I tank 1 residues produced by batch leaching calcines from two zinc plants outside North America with spent electrolyte and water at pH 1.5. Most residue samples were filtered and washed directly although in some tests, the residue was flocculated with 40 g/t Percol 351 (non-ionic, Allied Colloid) prior to filtration and washing. Rougher flotation was then carried out with well-washed residue at pH 3.0-3.5 with 200 g/t R-3501 (dithiophosphate) and 100 g/t S-4037 (thionocarbamate) added in stages. Two stages of cleaning were used with small dosages of collector.

TABLE XVI

SILVER BALANCE IN LOCKED CYCLE FLOTATION TESTS USING COMPOSITE KIDD CREEK RESIDUE OBTAINED AT pH 1.5

	Charge		Concentrate			Rougher Tails		Cleaner Tails (calculated)		Recovery,%	
Cycle	Wt.g	% Ag	Wt.g	% Ag	% Zn	Wt.g	% Ag	Wt.g	% Ag	Ag	Zn
1	1083.1	0.0465	38.6	0.921	43.4	904.5	0.0097	140.0	0.0431	80.0	5.0
2	1085.1	0.0461	41.8	0.932	40.3	1040.2	0.0096	141.5	0.0537	80.2	8.3
3	1085.3	0.0472	44.6	0.919	40.6	1039.4	0.0091	141.2	0.0623	81.2	10.0
4	1085.3	0.0471	43.9	0.955	40.3	998.9	0.0084	182.1	0.0405	82.7	11.0
5	1085.1	0.0450	43.1	0.962	41.3	1053.3	0.0091	169.2	0.0394	81.5	9.8
Average			-	0.938	41.1	-	0.0093	-	-	81.6	8.8

Flotation of the residue (0.15% Ag) from calcine A resulted in silver recoveries of 86-88% to twice-cleaned concentrates assaying 2.2-2.3% Ag and 55-57% Zn (Table XVII). Over 14% of the zinc in the residue was floated along with the silver, and this suggests that calcine A contained a large amount of unroasted sphalerite.

The residue from calcine B responded somewhat differently. The rougher silver recoveries were 73.6% for unflocculated and 62.6% for flocculated residue (Table XVIII). The twice-cleaned silver concentrates assayed 2.27% Ag and 1.62% Ag with recoveries of 44.3% and 57.2% for flocculated and unflocculated feed, respectively.

The results with these two different calcine samples indicate that, although very similar concentrate grades could be obtained, the flotation responses were quite different, possibly because of different mineral forms of silver in the two residues.

4.2.3 Low Acid Leach Residues

Samples of low acid leach (LAL) residue, were prepared in the CEZ pilot plant by subjecting CEZ and Kidd Creek calcines to a three-stage neutral leach, followed by thickening and a low acid leach at pH 1.5. These residues then were used in a series of flotation tests to characterize the floatability of silver. The leach conditions and complete residue and calcine assays are given in Tables XIX and XX. The residue assays show a significant variation in composition with the leach conditions, and hence, the mineralogical compositions may be different from residue to residue.

Rougher and cleaner flotation tests (flotation of well-washed residue at pH 3.5-4.0 with reagents R-3501 and S-4037) showed very poor silver floatability with all LAL residues (less than 60% recovery in roughing). The cleaning efficiency was also poor, and silver recoveries

TABLE XVII

FLOTATION OF NEUTRAL LEACH RESIDUE (pH 1.5) PRODUCED FROM CALCINE A

Products	Wt %	Assay, %				Distribution, %	
		Ag		Zn		Ag	Zn
		Stage	Cum.	Stage	Cum.		
Calcine A, NL-I Tank 1, flocculated, washed. Flotation at pH 3.5							
Conc.	5.66	2.25		54.8		86.7	14.3
Cl.2 Tail	5.94	0.054	1.125	19.7	41.9	2.2	5.4
Cl.1 Tail	24.98	0.025	0.374	19.5	26.6	4.3	22.4
Rgh. Tail	63.42	0.016		19.8		6.9	57.9
HEADS	100.00	0.147		21.7		100.0	100.0
Calcine A, NL-I Tank 1, unflocculated, washed. Flotation at pH 3.5							
Conc.	5.68	2.29		56.8		87.8	14.4
Cl.2 Tail	2.42	0.066	1.626	19.3	45.6	1.1	2.1
Cl.1 Tail	16.57	0.027	0.552	19.5	28.1	3.0	14.5
Rgh. Tail	75.33	0.016		20.5		8.1	69.0
HEADS	100.00	0.148		22.4		100.0	100.0

TABLE XVIII

FLOTATION OF NEUTRAL LEACH RESIDUE (pH 1.5) PRODUCED FROM CALCINE B

Products	Wt %	Assay, %				Distribution, %	
		Ag		Zn		Ag	Zn
		Stage	Cum.	Stage	Cum.		
Calcine B, NL-I Tank 1, flocculated, washed. Flotation at pH 3.0							
Conc.	0.98	2.27		32.5		44.3	2.0
Cl.2 Tail	1.57	0.16	0.97	14.5	21.4	5.0	1.4
Cl.1 Tail	11.97	0.056	0.217	18.5	19.0	13.3	13.8
Rgh. Tail	85.48	0.022		15.6		37.4	82.8
HEADS	100.00	0.0503		16.1		100.0	100.0
Calcine B, NL-I Tank 1, unflocculated, washed. Flotation at pH 3.0							
Conc.	2.37	1.62		21.9		57.2	3.1
Cl.2 Tail	2.68	0.11	0.818	15.7	18.6	4.4	2.5
Cl.1 Tail	14.61	0.055	0.251	18.3	18.4	12.0	15.9
Rgh. Tail	80.34	0.022		16.4		26.4	78.5
HEADS	100.00	0.0670		16.8		100.0	100.0

TABLE XIX

CALCINE LEACH CONDITIONS[1] FOR THE PRODUCTION OF LOW ACID LEACH RESIDUES

Calcine Source	Residue Sample	Neutral Leach[2]	Low Acid Leach
CEZ	17	Spent + LAL O/F, pH 1.5 → 4.0	Spent + water at pH 1.5
	18	Spent + LAL O/F, pH 1.5 → 4.0	Jarosite O/F (no solids) + spent pH 1.5
	19	Spent + LAL O/F, pH 1.5 → 4.0	Jarosite O/F (130 g/L solids) + spent pH 1.5
	20	Spent + LAL O/F, pH 3.0 → 4.0	Spent + water at pH 1.5
KCM	21	Spent + LAL O/F, pH 1.5 → 4.0	Spent + water at pH 1.5

[1] See Appendix I for detailed leach procedures.

[2] pH range corresponds to pH range from tank 1 to tank 3 of the neutral leach.

TABLE XX

LOW ACID LEACH RESIDUE ASSAYS

Calcine Source	Residue Sample	Zn	Fe	Pb	Ag	S_T	$S(SO_4)$	$S(S^=)$
CEZ								
	17	20.2	37.5	9.42	0.037	2.61	1.82	0.79
	18	20.2	37.6	7.29	0.037	3.08	2.24	0.84
	19	9.54	33.7	-	0.025	9.23	8.35	0.88
	20	22.0	38.3	-	0.030	2.95	1.55	1.44
KCM								
	21	18.7	38.7	2.49	0.036	2.88	1.88	1.0

to twice-cleaned concentrates were generally less than 30% (Table XXI). It is believed that the poor floatability is caused by precipitation of iron and other metals during neutralization in tank 3 of the neutral leach. Clearly, the acidity in the LAL (pH 1.5, ~15 gpL H_2SO_4) is not sufficient to overcome the damage done in neutral leaching.

4.2.4 High Acid Leach Residue

Three of the above low acid leach residues (Section 4.2.3), originating from CEZ calcine, were subjected to a hot acid leach at 95°C and 100 g/L H_2SO_4 for 6 h to generate HAL residue for flotation studies. The residues were filtered, washed and floated with reagents R-3501 and S-4037 at the natural pH (pH 2.5-3.0). The leach conditions and flotation results are summarized in Table XXII.

Flotation of the HAL residue obtained by leaching LAL residue with spent electrolyte and water, gave a twice-cleaned concentrate assaying 1.37% Ag with only 22.6% silver recovery. The rougher silver recovery was 70.2%, but the cleaning efficiency was very poor (Test 173). On the other hand, flotation of HAL residue obtained by leaching LAL residue with spent and jarosite O/F gave a cleaner concentrate assaying 2.14% Ag with 66.5% silver recovery. The rougher recovery was 80.5% (Test 174). The HAL residue produced from residues generated at high pH in the neutral leach gave higher silver recoveries, but the cleaner concentrate assayed only 0.55% Ag, indicating co-flotation of fines (Test 175). The reasons for the large differences in silver selectivity during flotation of HAL residues, in which the preceding LAL was performed with and without jarosite O/F, are not known.

4.2.5 Discussion

The silver flotation studies conducted with the various process residues, originating from different calcine sources, have indicated that silver floatability is predominantly affected by the leach conditions employed in residue generation. Slight variations in silver recovery were observed from one calcine to another, but this variation was much less significant than the impact of the leach parameters.

TABLE XXI

FLOTATION OF LOW ACID LEACH RESIDUE

Test No.	Residue Sample	Neutral Leach			LAL[1]		Assay, %						Recovery, %			
		LAL O/F	pH Tank 1	pH Tank 3	Spent	Jarosite O/F	Cl. 2 Conc.		Cl. 1 Conc.	Rougher Conc.	Rougher Tail	Heads	Cl. 2 Conc.		Cl. 1 Conc.	Rougher Conc.
							Ag	Zn					Ag	Zn		
139	17	Y	1.5	4.0	Y	N	0.18	47.8	0.167	0.107	0.023	0.0404	17.9	5.0	31.7	55.8
142	17	Y	1.5	4.0	Y	N	0.40	36.4	0.277	0.10	0.022	0.0405	22.6	3.6	40.0	52.5
140	18	Y	1.5	4.0	Y	Y	0.36	33.0	0.224	0.10	0.023	0.0416	24.5	4.2	35.7	58.1
144	19	Y	1.5	4.0	Y	Y[2]	0.51	37.7	0.20	0.048	0.016	0.0240	28.1	5.6	32.2	49.6
145	20	Y	3.0	4.0	Y	N	0.40	49.5	0.31	0.114	0.014	0.0310	32.2	5.2	43.1	62.0
146	21	Y	1.5	4.0	Y	N	0.93	59.8	0.66	0.111	0.021	0.0352	29.9	3.2	35.2	49.8

[1] Leached at pH 1.5 (∿15 gpL H_2SO_4.

[2] Jarosite O/F used in LAL contained high level of jarosite solids.

TABLE XXII

FLOTATION OF HIGH ACID LEACH RESIDUES

Test No.	Residue	Neutral Leach			LAL[1]		HAL[2]	Assay, % Ag					Ag Recovery, %		
		LAL O/F	pH Tank 1	pH Tank 3	Spent	Jarosite O/F		Cl. 2 Conc.	Cl. 1 Conc.	Rougher Conc.	Rougher Tail	Heads	Cl. 2 Conc.	Cl. 1 Conc.	Rougher Conc.
173	22	Y	1.5	4.0	Y	N	Y	1.37	1.03	0.417	0.08	0.183	22.6	35.4	70.2
174	23	Y	1.5	4.0	Y	Y	Y	2.14	1.367	0.445	0.056	0.189	66.5	70.2	80.5
175	24	Y	3.0	4.0	Y	N	Y	0.55	0.36	0.222	0.053	0.143	64.2	73.5	82.5

[1] Leached at pH 1.5

[2] HAL was done at 95°C for 6 h with 100 gpL H_2SO_4

Comparative analysis of silver grade-recovery relationships determined with neutral leach tank 1, neutral leach tank 3, low acid leach and high acid leach residue indicates that high acid leach residue and neutral leach tank 1 residue (pH 1.5) are vastly superior feeds to silver flotation than the neutral leach tank 3 and the low acid leach residues (Figures 19-21). Flotation of high acid leach residue is practiced commercially as a means of upgrading the silver concentrate; in a plant with an existing HAL circuit, flotation of this residue is attractive. For a zinc plant without a high acid leach circuit, flotation of neutral leach residue could provide an attractive alternative to the installation of a high acid leach or a jarosite retreatment process.

Mineralogical analysis of flotation concentrates, produced from "high-silver" (Calcine A) and "low-silver" (CEZ Calcine) neutral leach residues, have shown that the flotation concentrates consist principally of sphalerite, with lesser amounts of zinc ferrite and $PbSO_4$ (Appendix II). Silver occurs mostly as Ag_2S or (Ag,Cu)S rims on sphalerite, although other sulphide associations of silver and copper are also present. Silver chloride was not detected. These studies suggest that the silver dissolves during neutral leaching and subsequently reacts with any unroasted sphalerite or other sulphides to form readily floatable silver sulphide.

4.3 Effect of Flotation Media on Silver Flotation

4.3.1 Dilute Leach Liquor

Recovery of silver from neutral leach residue by flotation would require that the residue be removed from the neutral leach circuit in a liquid/solid separation step, washed to some degree, floated to recover silver, and finally returned to the main leach circuit for the recovery of zinc present in the residue as zinc ferrite.

Since water balance is a concern in most zinc plants, an investigation of the effect of flotation medium composition on residue flotation

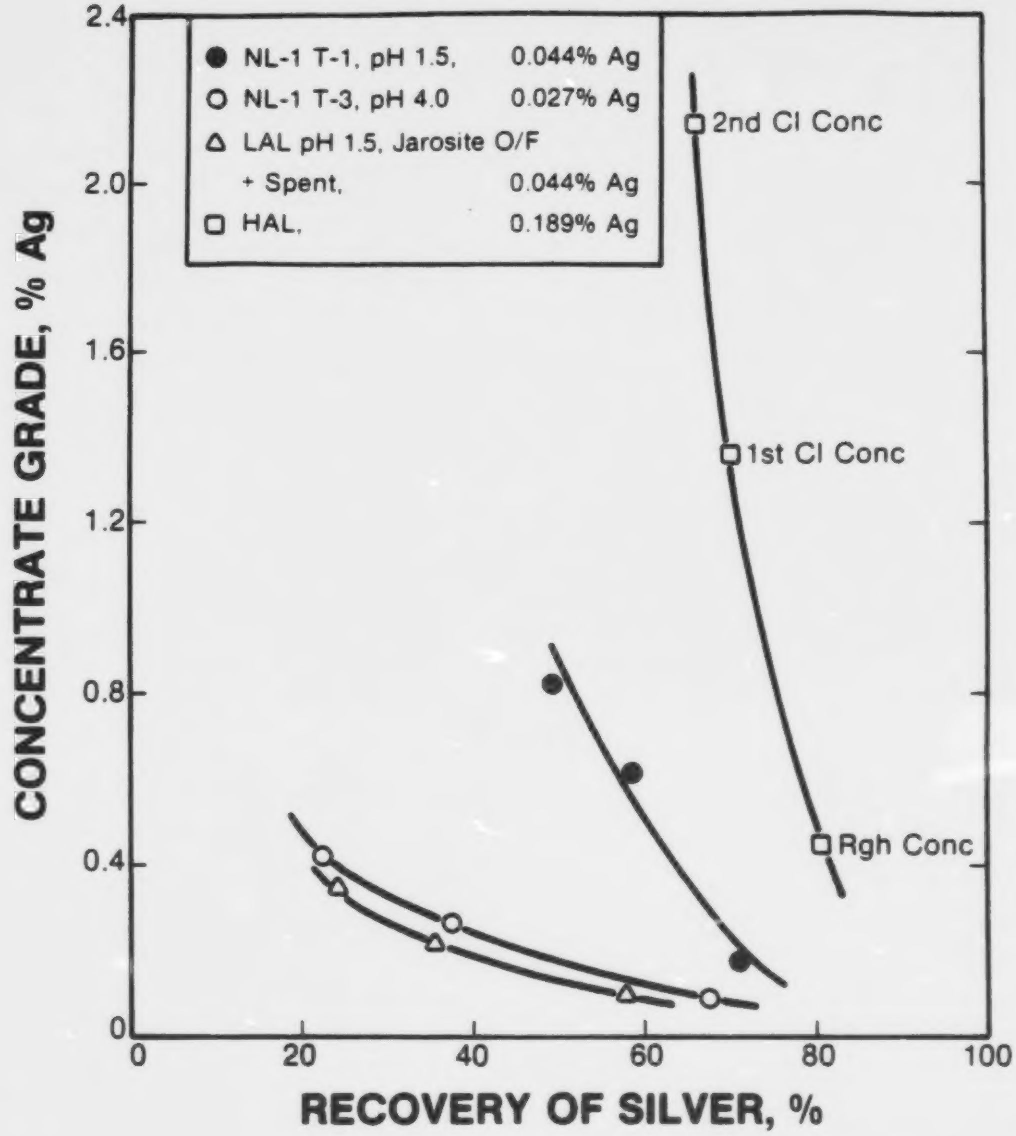

Figure 19. Silver grade and recovery during cleaning of NL-I tank 1, NL-I tank 3, LAL and HAL residues produced from CEZ calcine. (The LAL residue was generated by leaching with spent and jarosite overflow. All other residues were generated using spent + water).

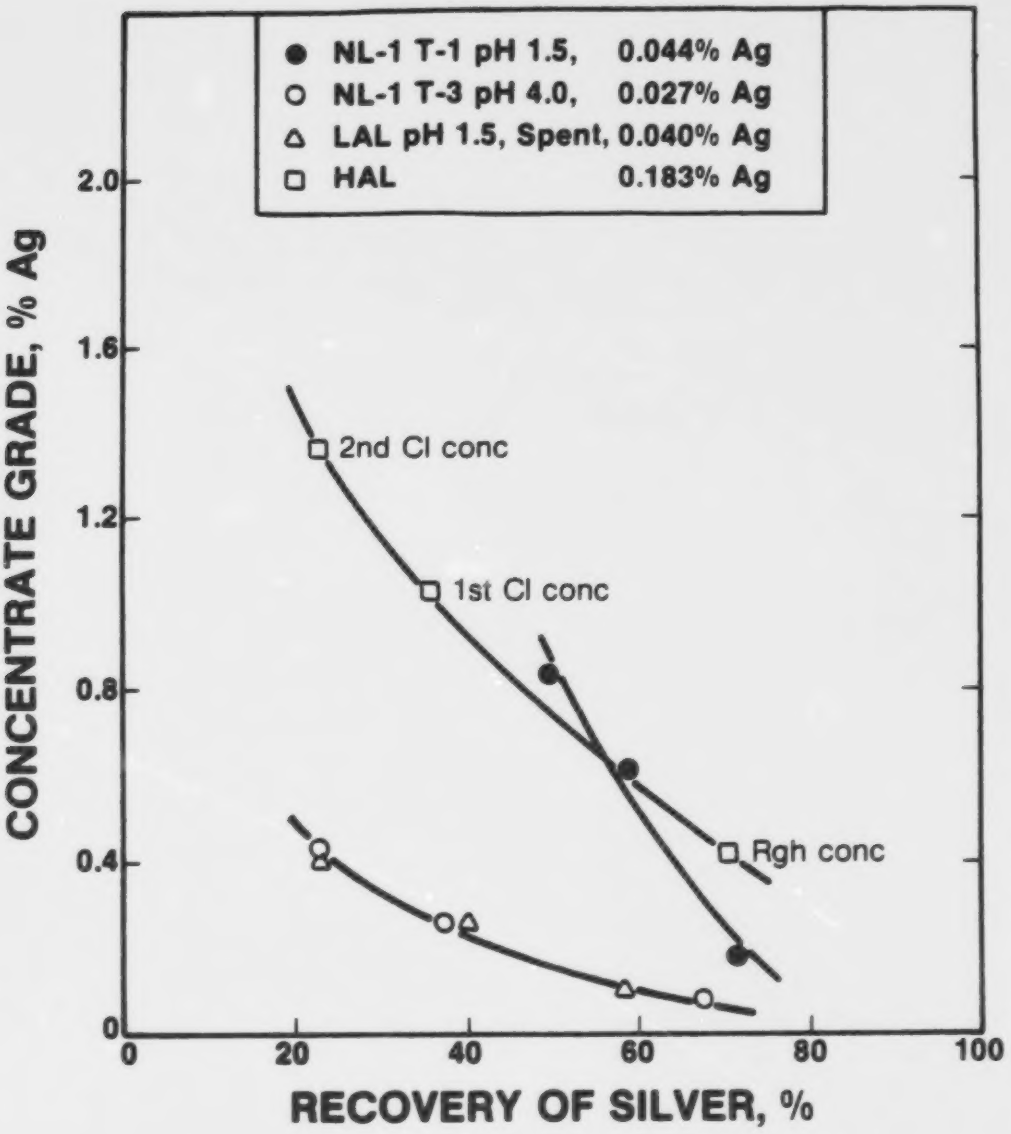

Figure 20. Silver grade and recovery during cleaning of NL-I tank 1, NL-I tank 3, LAL and HAL residues produced from CEZ calcine. (All residues were generated by leaching with spent + water)

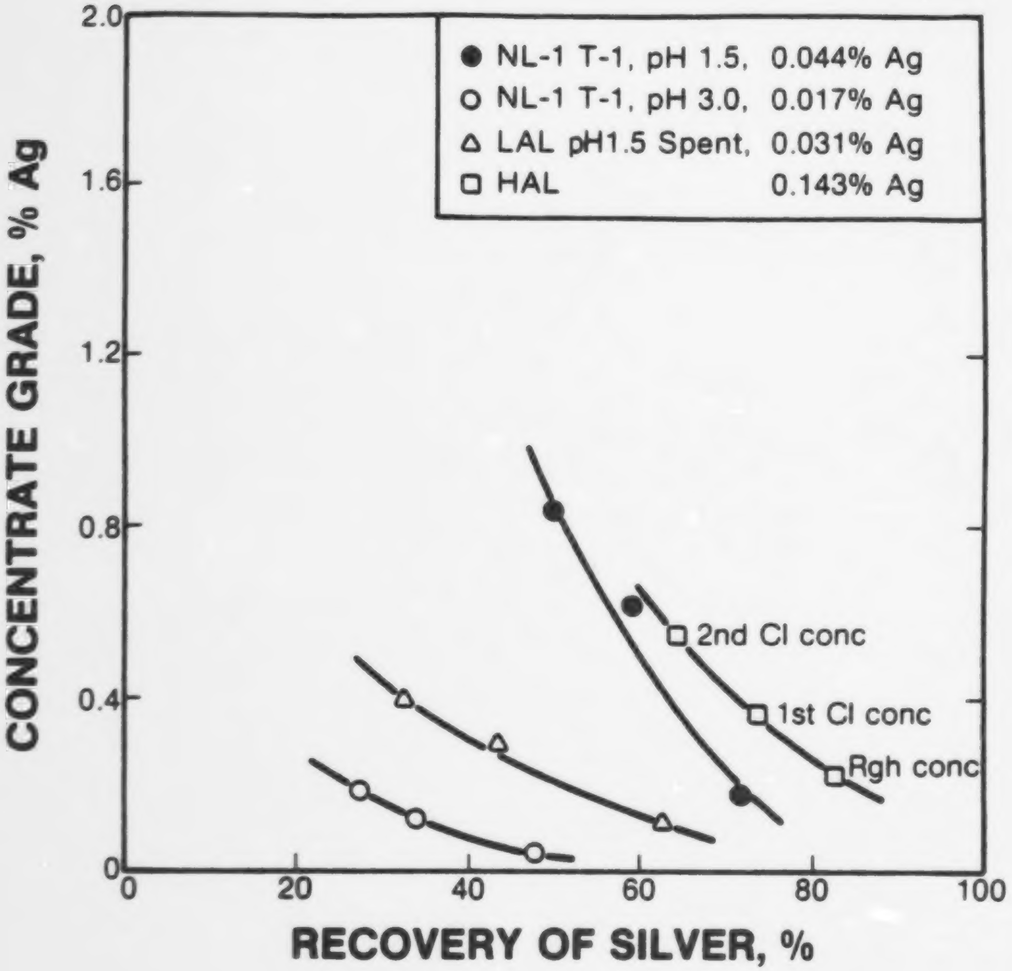

Figure 21. Silver grade and recovery during cleaning of NL-I tank 1, NL-I tank 3, LAL and HAL residues produced from CEZ calcine. (All residues were generated by leaching with spent + water)

was undertaken to shed some light on the amount of electrolyte dilution that would have to be achieved by residue washing.

A series of flotation tests was conducted with a sample of neutral leach tank 1 residue (0.036% Ag, 23.5% Zn, 37.2% Fe, 7.7% Pb, 0.45% $S^=$) prepared from CEZ calcine and (i) neutral leach tank 1 liquor (85 g/L Zn, 1.0 g/L Fe, 14 g/L H_2SO_4) diluted to give solutions containing 1-60 g/L Zn, and (ii) 30 g/L Zn solution prepared from reagent grade zinc sulphate. In each test, the residue was slurried at 25% solids, conditioned* at the specified pH with 100 g/tonne $Na_2S \cdot 9H_2O$ for 10 min., and then conditioned for a further 10-min. with 100 g/tonne dithiophosphate (R-3501, American Cyanamid Co.). Rougher flotation was conducted for 20 min., with stage addition of collector and frother (AF-65). Four incremental 5-min. froth cuts were taken.

The results of the initial flotation tests (Figure 22, Table XXIII) show that the silver selectivity decreased markedly with increasing leach liquor content in the flotation medium, and that there was virtually no selectivity at >30 g/L Zn. However, since the pH of the flotation medium varied with the degree of leach liquor dilution (Table XXIII, tests 36-30), additional tests were performed with (i) diluted leach liquor at 32 and 59 g/L Zn in which the pH was adjusted to 3.8 with ammonia, and (ii) reagent grade $ZnSO_4$ solution at 31 g/L Zn and pH 3.8. The results (Table XXIII, tests 80-82) show a further reduction in silver selectivity when using neutralized diluted leach liquor, and this is possibly due to the precipitation of iron. Silver floatability in the reagent grade solution was much improved over that observed with leach liquors diluted to 30 g/L Zn.

As these results suggest that zinc concentration per se does not seem to have a strong negative effect on silver floatability, an investigation was initiated to evaluate the effect of other metals typically

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* Chronologically, these tests were conducted before those already reported in which it was shown that sulphidization with Na_2S was detrimental to silver flotation.

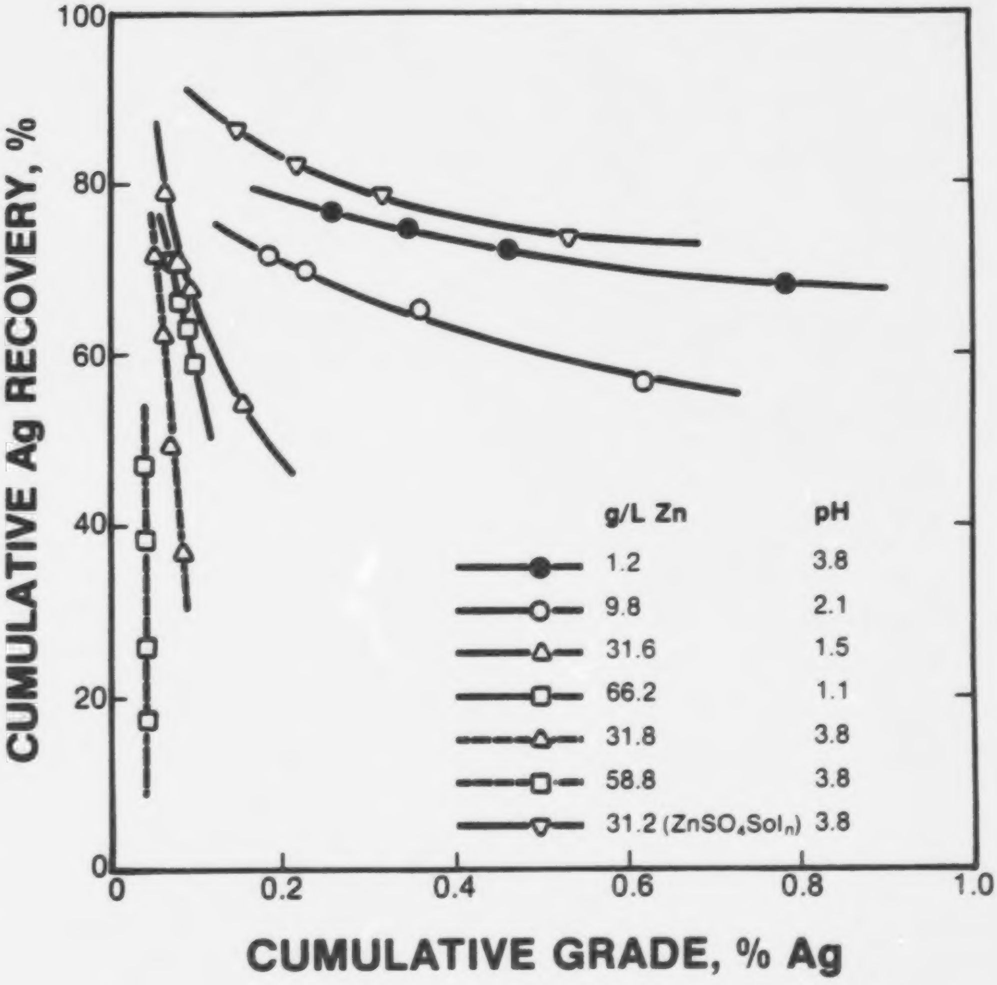

Figure 22. Effect of flotation medium composition on silver recovery and grade during rougher flotation of neutral leach residue.

TABLE XXIII

EFFECT OF FLOTATION MEDIUM ON SILVER EXTRACTION

Test No.	Flotation Medium[1]			20-min. Rgh. Concentrate	
	pH	Zn gpL	Fe mgpL	Grade % Ag	Recovery %
T-36, residue + diluted leach liquor	3.8	1.21	42	0.255	77.0
T-37, residue + diluted leach liquor	2.1	9.8	110	0.184	73.3
T-38, residue + diluted leach liquor	1.5	31.6	210	0.068	79.1
T-39, residue + diluted leach liquor	1.1	66.2	430	0.077	70.8
T-80, residue + diluted leach liquor, neutralized to pH 3.8	3.8	31.8	45	0.057	71.5
T-81, residue + diluted leach liquor, neutralized to pH 3.8	3.8	58.9	74	0.041	47.6
T-82, residue + $ZnSO_4$ solution at pH 3.8	3.8	31.2	52	0.143	86.1

[1] Flotation medium was analyzed after roughing.

found in zinc electrolyte.

4.3.2 Synthetic Electrolyte

A series of silver flotation tests was carried out using well-washed neutral leach tank 1 residue (0.046% Ag, 23.9% Zn, 41.3% Fe and 3.6% Pb) obtained by leaching Kidd Creek calcine on a continuous basis at the CEZ pilot plant. The primary flotation medium was a zinc sulphate solution prepared with distilled water and adjusted to pH 1.5 with sulphuric acid. Subsequently, $MnSO_4$ (2.5 gpL Mn^{++}), $MgSO_4$ (0.5 gpL Mg^{++}), $CaSO_4 \cdot 2H_2O$ (0.5 gpL gypsum), $CuSO_4$ (0.1 gpL Cu^{++}). $Fe_2(SO_4)_3$ (1.5 gpL Fe^{+3}) and Na_2SiO_3 (0.1 gpL SiO_2) were added to the flotation medium. The well washed leach residue was repulped with the flotation medium at 25-30% solids, and rougher flotation was carried out for 15 min. with 200 g/t R-3501 (dithiophosphate) and 100 g/t S-4037 (thionocarbamate) added in stages. Two stages of cleaning were employed with small dosages of collector. In some tests, the slurry pH was adjusted to 3.5 in residue repulping prior to flotation. Flotation medium samples were taken after 5 min. of repulping to determine if there was any significant precipitation of the added metals or dissolution of metals from the residue.

The flotation results (Tables XXIV, XXV) clearly show that the dissolved elements in the flotation medium do not affect silver flotation within the range examined and at pH 1.5. Rougher silver recoveries of over 85% were obtained, and twice-cleaned concentrates assaying about 0.6% Ag were produced at recoveries of over 75%. However, when the pulp pH was adjusted to 3.5, rougher recoveries were reduced by 5-15%. The largest negative effects were observed at pH 3.5 in the presence of ferric ion, which would have precipitated during neutralization from pH 1.5 to 3.5. These results indicate that dissolved minor elements do not interfere with silver recovery as long as the pulp pH is maintained low enough to prevent their precipitation.

TABLE XXIV

EFFECT OF MINOR ELEMENTS IN THE FLOTATION MEDIUM OF SILVER FLOATABILITY

Test No.	Targeted Flotation Medium g/L and pH		Assay, % Ag				Ag Recovery, %		
			Rgh Conc.	Rgh Tails	Cl.1 Conc.	Cl.2 Conc.	Rgh Conc.	Cl.1 Conc	Cl.2 Conc.
161	30 g/L Zn	pH 1.5	0.146	0.0073	0.333	0.53	86.6	79.1	76.7
162	T-161, 2.5 g/L Mn^{++}	pH 1.5	0.137	0.0068	0.332	0.57	87.0	80.5	77.2
163	T-162, 0.5 g/L Mg^{++}	pH 1.5	0.154	0.0071	0.377	0.61	85.9	78.9	74.9
164	T-163	pH 3.5	0.168	0.011	0.397	0.57	79.0	68.3	62.7
165	T-163, 0.5 g/L gypsum	pH 1.5	0.166	0.0081	0.392	0.61	85.1	77.2	73.4
166	T-165, 0.1 g/L Cu^{++}	pH 1.5	0.153	0.0071	0.354	0.60	87.0	79.8	75.1
167	T-166	pH 3.5	0.135	0.012	0.334	0.59	79.6	71.4	67.3
168	T-166, 1.5 g/L Fe^{+3}	pH 1.5	0.164	0.008	0.394	0.62	85.2	77.1	73.8
169	T-168		0.151	0.008	0.386	0.62	85.0	79.6	73.9
170	T-168	pH 3.5	0.122	0.015	0.248	0.43	71.8	66.0	62.5
171	T-169		0.117	0.015	0.282	0.50	71.8	67.0	64.4
172	T-168, 0.1 g/L SiO_2	pH 1.5	0.154	0.0072	0.343	0.55	86.1	79.2	75.1

TABLE XXV

CHEMICAL ANALYSIS OF FLOTATION MEDIUM

Test No.	Targeted Flotation Medium g/L and pH							pH	Flotation Medium Assay[1], g/L					
	Zn	Mn	Mg	Gypsum	Cu	Fe	SiO_2		Zn	Fe	Cu	Mn	Mg	SiO_2
161	30							1.5	28.0	0.012	0.005	0.003	0.012	0.009
162	30	2.5						1.5	29.0	0.014	0.005	2.50	0.012	ND
163	30	2.5	0.5					1.5	28.5	0.011	0.005	2.71	0.42	ND
164	30	2.5	0.5					3.5	29.3	0.003	0.003	2.81	0.45	ND
165	30	2.5	0.5	0.5				1.5	30.7	0.014	0.005	2.88	0.47	ND
166	30	2.5	0.5	0.5	0.1			1.5	29.4	0.011	0.11	2.77	0.45	ND
167	30	2.5	0.5	0.5	0.1			3.5	28.0	0.003	0.11	2.67	0.45	ND
168	30	2.5	0.5	0.5	0.1	1.5		1.5	27.8	1.35	0.12	2.74	0.45	ND
169	30	2.5	0.5	0.5	0.1	1.5		1.5	28.0	1.36	0.12	2.81	0.45	ND
170	30	2.5	0.5	0.5	0.1	1.5		3.5	28.2	0.09	0.11	2.84	0.45	ND
171	30	2.5	0.5	0.5	0.1	1.5		3.5	27.4	0.20	0.10	2.53	0.44	ND
172	30	2.5	0.5	0.5	0.1	1.5	0.1	1.5	27.8	1.42	0.12	2.64	0.45	0.120

[1] Medium samples were taken after 5-min. conditioning.

4.4 Effect of Residue Flocculation

Leach residue preparation studies in the laboratory and pilot plant showed that, without flocculation, the neutral leach tank 1 residue was extremely difficult to settle and filter. With flocculation, however, the residue could be thickened and readily filtered in a press.

To examine the effect of flocculation on silver flotation, a series of flotation tests was carried out using flocculated and washed neutral leach tank 1 residue produced by leaching CEZ calcine II on a continuous basis in the pilot plant. Leaching was performed with spent electrolyte and water at pH 1.5 and 80°C. At the end of the leach the slurry was flocculated with Percol 351 (non-ionic polyacrylamide flocculant, Allied Colloids) at a rate of 10-40 g/tonne. The pulp was then filtered and washed on a filter press. Prior to conditioning, the filter cake was reslurried in either a high shear mixer (food blender) or a low shear mixer (flotation cell) at 50% solids and then was transferred to a 1 kg flotation cell for conditioning. The pulp was conditioned with R-3501 (dithiophosphate, American Cyanamid Co.) and S-4037 (thionocarbamate) in four stages (total 100 g/t each) and floated for 20 min. at about 35% solids with AF-65 frother as required. The rougher concentrate was cleaned twice, and a small dose of collector was used only in the first cleaning. Throughout the tests, dilute leach liquor (20 g/L Zn, 0.3 g/L Fe and pH 1.9) was used as the flotation medium to approximate the flotation liquor composition under equilibrium conditions in an operating circuit. One test was carried out without flocculant as a control.

The results (Table XXVI, Figure 23) show that flocculation with high shear repulping did not affect the silver selectivity or grade. Silver recoveries of 83-85% were obtained, after two cleanings, at grades of 0.6-0.7% Ag from a flotation feed containing 0.037% Ag. Silver recovery with low shear repulping was reduced by about 7%. The calculated silver head grade in the test with unflocculated residue is low when compared to those

TABLE XXVI

EFFECT OF RESIDUE FLOCCULATION ON SILVER FLOTATION

Test/ Products	wt. %	Assays, %				Recovery, %	
		Ag		Zn		Ag	Zn
		Stage	cumulative	stage	cumulative		
Test 182. No flocculation, high shear repulping							
Conc.	3.94	0.684		46.2		83.0	7.6
Cl 2, tail	1.44	0.044	0.513	23.8	40.2	2.0	1.4
Cl 1, tail	10.39	0.0137	0.184	23.0	28.9	4.4	9.9
Rgh. tail	84.23	0.0041		23.2		10.6	81.1
Heads	100.00	0.0325		24.1		100.0	100.0
Test 185. Flocculated, 10 g/t Percol 351, high shear repulping							
Conc.	4.23	0.719		39.6		84.3	7.0
Cl 2, tail	4.12	0.037	0.383	23.1	31.5	4.3	4.0
Cl 1, tail	19.10	0.0103	0.123	23.5	25.9	5.4	18.7
Rgh. tail	72.55	0.0033		23.2		6.0	70.3
Heads	100.00	0.0361		23.9		100.0	100.0
Test 184. Flocculated 30 g/t Percol 351, high shear repulping							
Conc.	5.37	0.588		38.5		84.9	8.6
Cl 2, tail	3.40	0.0306	0.372	23.5	32.7	2.8	3.3
Cl 1, tail	14.08	0.0101	0.149	23.7	27.1	3.8	13.8
Rgh. tail	77.15	0.0041		23.2		8.5	74.3
Heads	100.00	0.0372		24.1		100.0	100.0
Test 183. Flocculated, 40 g/t Percol 351, high shear repulping							
Conc.	4.44	0.703		42.5		84.2	7.7
Cl 2, tail	2.68	0.051	0.457	23.4	35.3	3.7	2.6
Cl 1, tail	11.21	0.0101	0.184	23.8	28.3	3.1	10.8
Rgh. tail	81.67	0.0041		23.7		9.0	78.9
Heads	100.00	0.0371		24.5		100.0	100.0
Test 186. Flocculated, 40 g/t Percol 351, low shear repulping							
Conc.	4.08	0.72		44.4		78.2	7.6
Cl 2, tail	1.98	0.084	0.51	23.0	37.4	4.4	1.9
Cl 1, tail	11.40	0.019	0.19	22.9	27.9	5.8	10.9
Rgh. tail	82.54	0.0053		23.1		11.6	79.6
Heads	100.00	0.0375		23.9		100.0	100.0

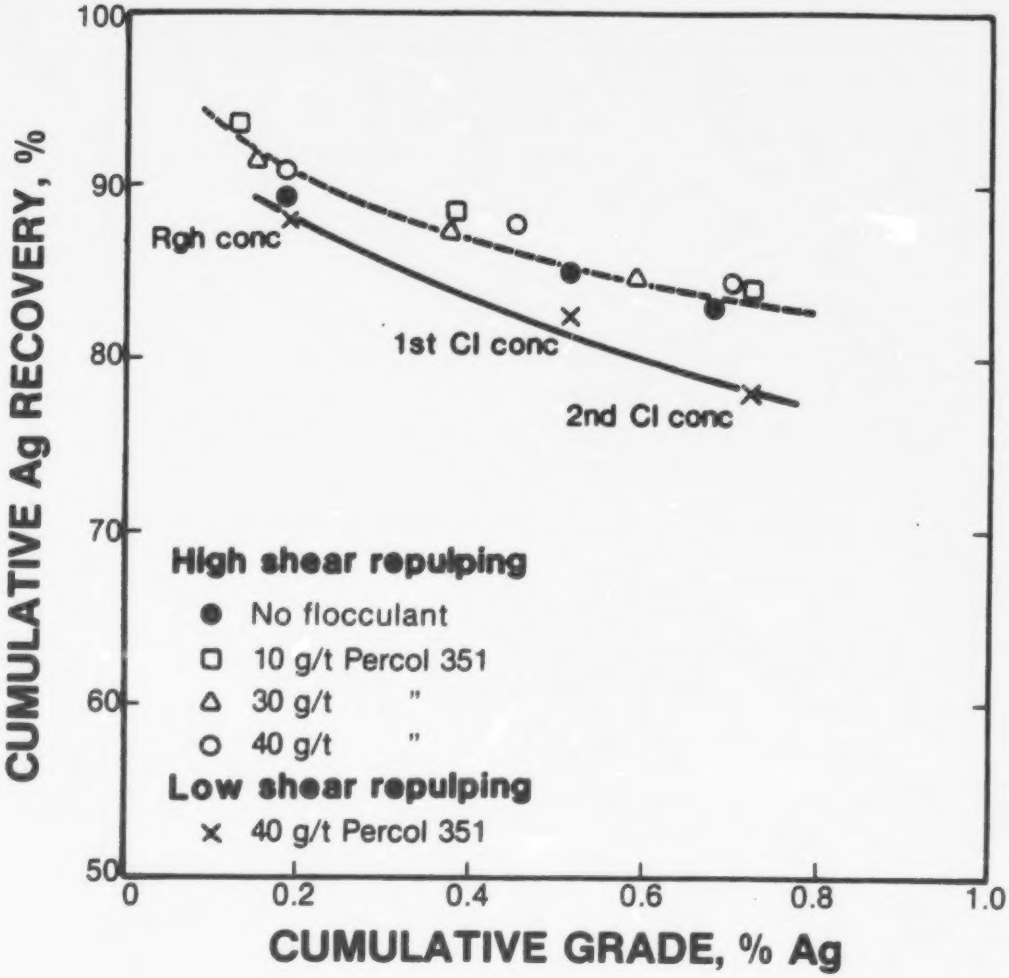

Figure 23. Effect of flocculant dosage on silver grade-recovery during roughing and cleaning of neutral leach residue.

for the flocculated residues. This suggests that the supernatant liquor contained fine suspended solids which were rich in silver, a fact which was confirmed by analysis of the suspended solids (0.31% Ag). Thus, flocculation is also required to prevent silver losses.

4.5 Locked Cycle Tests

A set of locked cycle flotation tests (6 cycles) was carried out with neutral leach residue produced on a continuous basis in the CEZ pilot plant by leaching CEZ calcine with spent electrolyte and water at pH 1.5. The leach residue was flocculated with 40 g/tonne Percol 351, filtered, washed and reslurried with diluted leach liquor (34 g/L Zn, 0.5 g/L Fe, 0.9 g/L Mn, 0.1 g/L Cu, pH 1.9) with high shear repulping. Rougher flotation and two stages of cleaning were conducted in laboratory scale cells with reagents R-3501 and S-4037 as described above. The cleaner tails from each stage were combined and returned to the repulping step for the following cycle.

The locked cycle system stabilized quickly and demonstrated the production of good silver concentrates at high recoveries (Tables XXVII and XXVIII). Projected concentrate grades are 0.6% Ag and 40% Zn at 85% silver recovery.

Mineralogical examination (Appendix II) of the flotation concentrate from the sixth cycle showed that the concentrate was comprised of sphalerite, with lesser amounts of zinc ferrite and $PbSO_4$. Silver was present as Ag_2S grains in elemental sulphur and/or silica gel and as Ag_2S rims on sphalerite. A few grains of gold also were observed in the concentrate, and the gold content could be economically significant.

4.6 Process Flowsheet

A conceptual flowsheet for the flotation of silver from neutral leach residue is given in Figure 24. Neutral leach residue from a pH 1.5 leach is filtered, repulped to about 30% solids with recycle process

TABLE XXVII

LOCKED CYCLE FLOTATION TESTS WITH NEUTRAL LEACH RESIDUE

	wt. g	Assays, %						Distribution, %					
		Ag	Zn	Pb	Cu	$S^=$	$S(SO_4^=)$	Ag	Zn	Pb	Cu	$S^=$	$S(SO_4^=)$
Conc. 1	72.2	0.57	44.4	1.91	0.27	27.0	0.36	11.3	1.34	0.15	0.46	13.05	0.15
2	97.6	0.56	40.2	3.13	0.24	26.4	0.52	15.0	1.64	0.34	0.67	16.89	0.30
3	95.4	0.53	40.8	3.27	0.24	27.2	0.63	13.9	1.63	0.35	0.65	16.99	0.35
4	153.3	0.36	33.4	5.81	0.33	18.2	0.98	15.2	2.14	1.00	1.19	18.27	0.88
5	94.7	0.54	38.3	3.32	0.30	27.6	0.59	14.1	1.52	0.35	0.67	17.11	0.33
6	79.9	0.64	42.2	1.93	0.27	28.2	0.40	14.0	1.41	0.18	0.51	14.76	0.19
Total	593.1	0.512	39.02	3.56	0.30	25.0	0.63	83.5	9.68	2.37	4.15	97.05	2.20
Tail 1	1328.5	0.0067	22.8	9.05	0.43	0.04	1.69	2.45	12.67	13.48	13.49	0.35	13.18
2	1405.5	0.0060	23.8	9.21	0.44	0.04	1.74	2.32	14.00	14.52	14.60	0.37	14.35
3	1441.0	0.0055	23.5	9.21	0.44	0.06	1.72	2.18	14.17	14.88	14.98	0.57	14.55
4	1458.0	0.0052	23.0	9.26	0.44	-	1.76	2.08	14.03	15.14	15.14	-	15.06
5	1654.5	0.0056	22.5	9.48	0.43	0.02	1.85	2.55	15.58	17.59	16.80	0.21	17.97
6	1757.6	0.0052	22.5	9.15	0.42	0.05	1.83	2.51	16.55	18.04	17.43	0.58	18.88
Total	9045.1	0.0056	22.98	9.23	0.43	0.035	1.77	14.09	87.00	93.66	92.44	2.08	93.99
2 Cl T6	50.4	0.074	22.6	9.93	0.42	1.42	1.64	1.03	0.48	0.56	0.50	0.47	0.48
1 Cl T6	308.0	0.016	22.0	9.86	0.40	0.20	1.84	1.35	2.84	3.41	2.91	0.40	3.33
Total	358.4	0.024	22.08	9.87	0.40	0.37	1.81	2.38	3.32	3.97	3.41	0.87	3.81
Cal. Heads	9996.6	0.0364	24.02	8.92	0.42	1.53	1.70	100.0	100.0	100.0	100.0	100.0	100.0
Projectn													
Ag Conc.	87.3	0.586	40.08	2.68	0.28	27.8	0.50	84.7	8.3	1.5	3.3	97.3	1.4
Tail	1706.1	0.0054	22.5	9.31	0.42	0.04	1.84	15.3	91.7	98.5	96.7	2.7	98.6
Feed	1793.4	0.0337	23.4	8.98	0.41	1.39	1.77	100.0	100.0	100.0	100.0	100.0	100.0

TABLE XXVIII

SILVER BALANCE IN LOCKED CYCLE FLOTATION TESTS

Cycle	Charge		Concentrate			Rougher Tails		Cleaner Tails (calculated)		Recovery[1] %
	wt. g	% Ag	wt.g	% Ag	% Zn	wt. g	% Ag	wt. g	% Ag	Ag
1	1667.8	0.0364	72.2	0.57	44.4	1328.5	0.0067	267.1	0.040	82.5
2	1668.8		97.2	0.56	40.2	1405.5	0.0060	432.8	0.019	84.4
3	1664.7		95.4	0.53	40.8	1441.0	0.0055	561.1	0.018	85.8
4[2]	1665.1		153.3	0.36	33.4	1458.2	0.0052	614.9	0.013	86.9
5	1664.0		94.7	0.54	38.3	1654.5	0.0056	529.7	0.016	85.5
6	1666.2		79.9	0.64	42.2	1757.6	0.0052	358.4	0.024	86.4
Avg.				0.512	39.0		0.0056			85.3

[1] Calculated using two-product formula.

[2] Second cleaning was improperly done: pulp overflowed due to limited cell size.

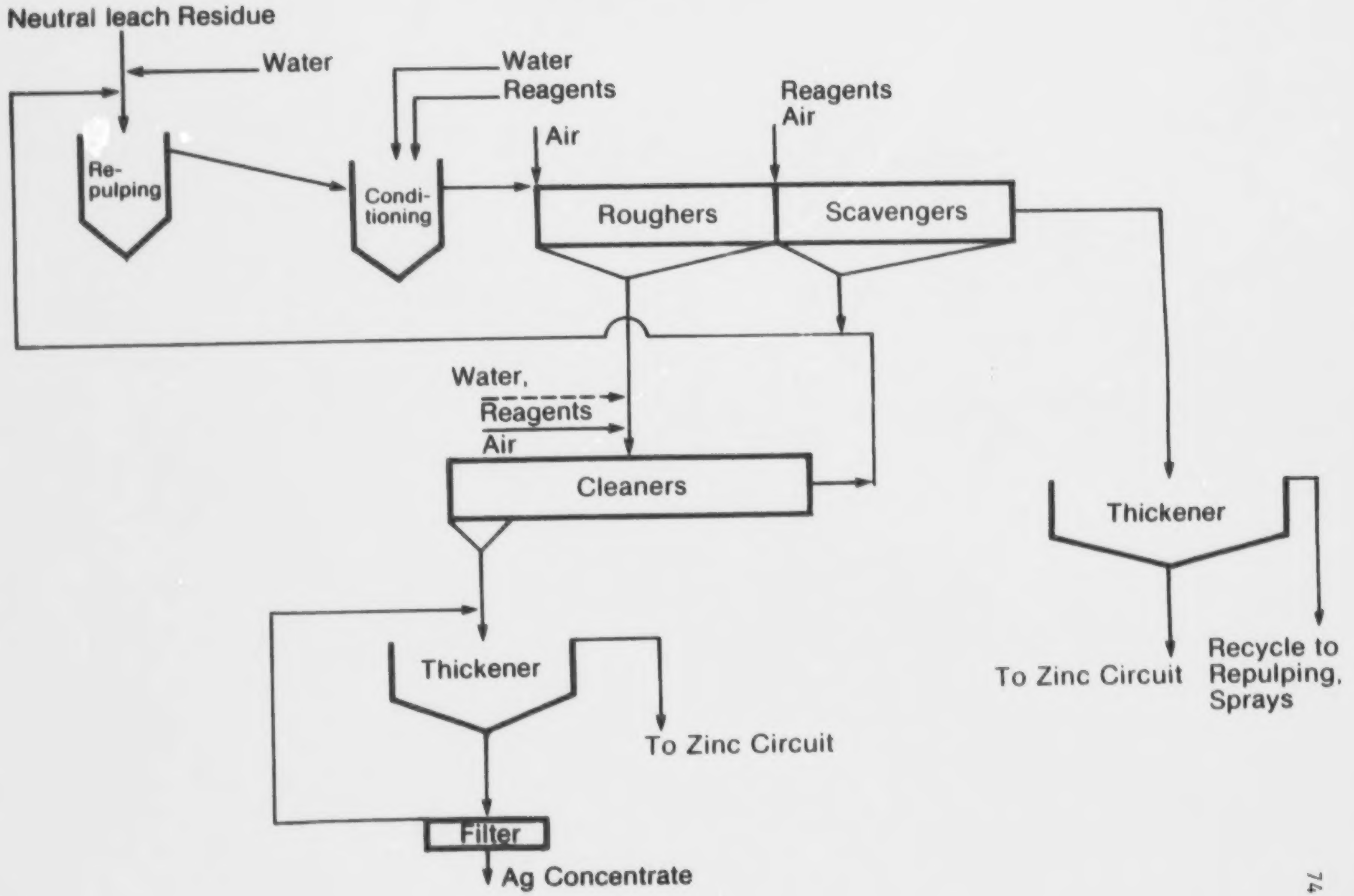
Neutral leach Residue
Water
Re-pulping
Water
Reagents
Condi-tioning
Air
Reagents
Air
Roughers
Scavengers
Water,
Reagents
Air
Cleaners
Thickener
To Zinc Circuit
Filter
Ag Concentrate
Thickener
To Zinc Circuit
Recycle to Repulping, Sprays

Figure 24. Conceptual flowsheet for flotation of neutral leach residue

streams and fresh water, and then is floated at 20-25% solids and pH 1.5-2.0 after conditioning. The rougher concentrate is cleaned, and the cleaner concentrate is thickened and filtered to yield a silver concentrate. The cleaner tails and a scavenger concentrate produced from the rougher tails are combined and recycled to repulping of the residue feed, so as to minimize water requirements. The flotation tails are thickened and the zinc ferrite-rich underflow is sent to acid leaching for zinc recovery. The scavenger tails thickener overflow solution is recycled for use in repulping and spray water.

The method of integration of such a flotation process into an existing zinc plant will be dependent upon a large number of site specific factors, and is beyond the scope of this investigation. One critical factor will be the plant water balance since flotation of an intermediate process residue will inevitably result in a net water input to the zinc plant. This factor will also impact on the residue L/S separation requirements and the degree of residue washing employed. The impact of silver flotation on the zinc operations must also be assessed, since while the value of the recovered silver will be significant, it is only a small fraction of the value of the zinc production. Consequently, the silver flotation process cannot impact negatively on zinc production.

5. SUMMARY AND CONCLUSIONS

Silver recovery from zinc plant leach residues by flotation is a viable process option provided that leach plant conditions are both understood and controlled to maintain the silver in the residue in a liberated and floatable form. Flotation of high acid leach residue is attractive for those plants with a HAL circuit, provided jarosite and silica gel formation in the HAL can be avoided.

Flotation of neutral leach residue is technically viable and merits consideration for those plants without a HAL circuit and having significant silver values in the feed. Residue leach conditions must be kept slightly acidic to promote the formation of Ag_2S, $(Ag,Cu)_2S$, and Ag_2S rims on residual unroasted sphalerite, while simultaneously avoiding the hydrolysis of soluble iron which depresses silver recovery and grade. Once the silver floatability has been depressed by iron hydrolysis in the neutral leach, it appears that a HAL step is required to restore floatability.

Silver flotation from neutral leach residues can be effected with conventional sulphide collectors. The flotation is slow and long roughing times are required. No benefit was identified in this study for conditioning the residue with zinc concentrate to "collect" non-sulphide silver in the residue. Sulphidization of the residue prior to flotation reduced silver floatability, and is to be avoided.

The silver flotation concentrate will require further processing to recover the silver values. Although concentrate treatment methods were not investigated, it is envisaged that the concentrate could be shipped to a lead smelter, or pressure leached on site in a batch autoclave to recover the contained zinc and to form a very high grade secondary silver-lead product. Other treatment methods can be envisaged, and process economics must be assessed for the various options

Work is required to assess the integration of a neutral leach residue flotation process into a specific existing plant, and to demonstrate the flotation operation at the pilot scale using actual plant residues. This work would define any required leach circuit modifications, liquid-solid separation requirements, process water requirements, allowable electrolyte levels in the flotation medium, sensitivity of silver flotation to upstream process upsets in the leach plant, flotation circuit operating characteristics and data required for the final process design.

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3. Beutier, D. and Predali, J.J., (to Societe Miniere et Metallurgique de Penarroya), Process for recovering silver from sulphate solutions, U.S. Patent 4,640,710, 3 February 1987.
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APPENDIX I

PROCEDURES FOR THE PREPARATION OF LEACH RESIDUE

APPENDIX I

Representative samples of neutral leach tank 1, neutral leach tank 3, low acid leach and high acid leach residues were prepared by leaching calcine in the pilot plant at CEZ. Specific neutral leach parameters investigated, in addition to the source of calcine, were the pH in the neutral leach tank 1, the recycle of LAL thickener O/F to tank 1 and the addition of zinc concentrate to tank 1 as a silver collector. The LAL and HAL residues were produced under fixed conditions, as the objective of these tests was primarily to determine if any loss in silver floatability during neutral leaching could be restored by subsequent acidic leach steps.

A. NEUTRAL LEACH TANK 1 RESIDUE

Neutral leach tank 1 residues were prepared on a continuous basis by leaching calcine at (i) pH 1.5 and 3.0, (ii) with and without zinc concentrate addition, and (iii) with and without LAL O/F additions, at 85°C with a 30-minute residence time.

Process Flowsheet and Equipment

The pilot plant flowsheet employed is shown in Figure A-1, while the process equipment employed is described below. (Equipment list numbers correspond to those shown in Figure A-1.

1. leach tank

12" H x 25" D SS V = 96.5 L

overflow : 10" H V = 80.4 L
3/4" ID pipe
1" from bottom

mixer : Lightnin
1/3 hp @ 1725 rpm

turbine : 4 bladed axial 6" D 45°

baffles : 2" W x 10" H
0.5" from side
1" from bottom

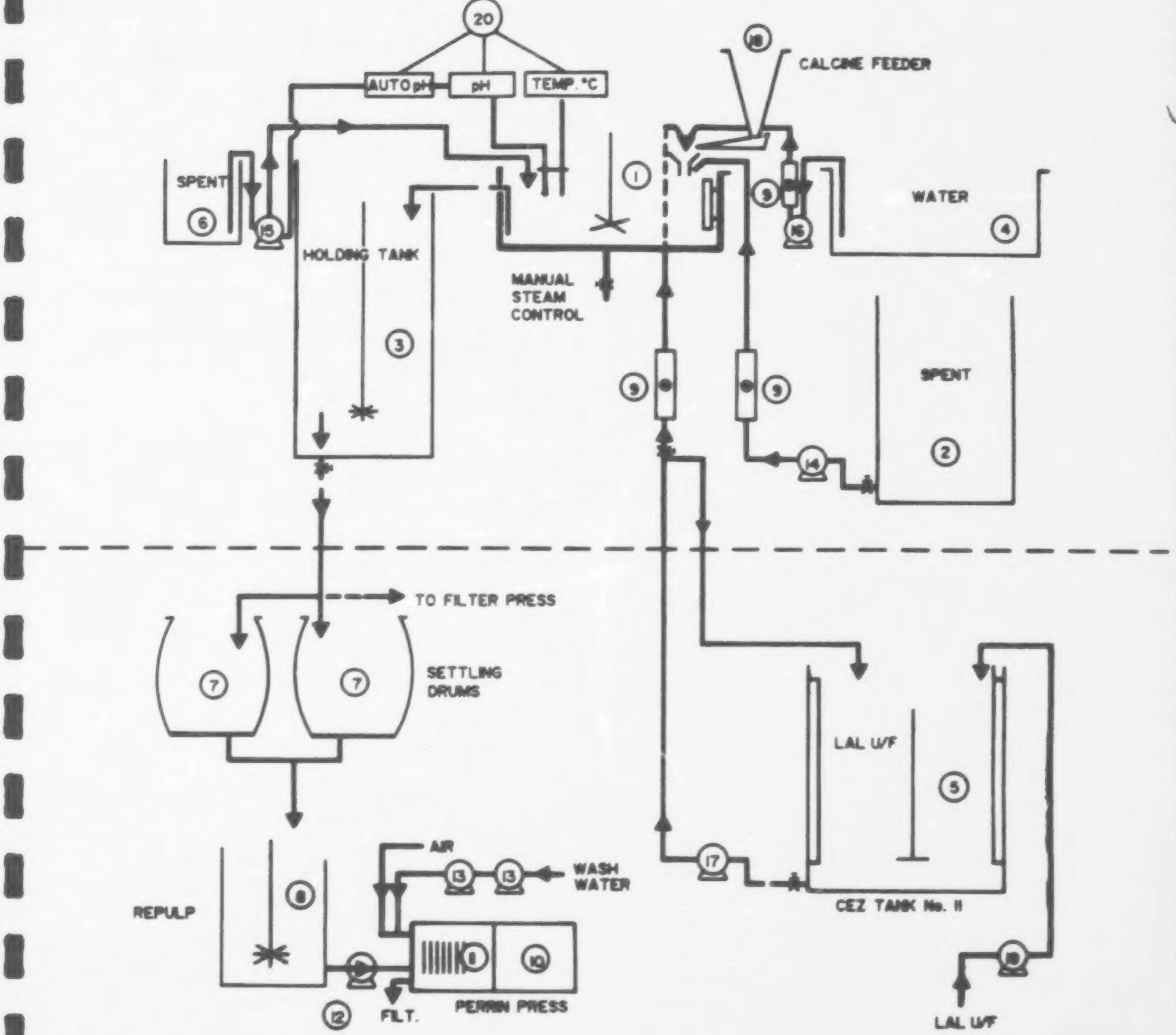
20
AUTO pH
pH
TEMP. °C
18
CALCINE FEEDER
SPENT
6
15
HOLDING TANK
3
1
MANUAL
STEAM
CONTROL
9
16
WATER
4
9
9
SPENT
2
14
TO FILTER PRESS
7
7
SETTLING
DRUMS
LAL U/F
5
17
CEZ TANK No. 11
19
LAL U/F
AIR
13
13
WASH
WATER
REPULP
8
11
10
12
FILT.
PERRIN PRESS

Figure A-1 C.E.Z. PILOT PLANT FLOWSHEET

2. spent tank

   37" H x 18.0" D Polyethylene V = 154.3 L

3. holding tank

   48" H x 18" D SS V = 200.2 L

4. water tank

   12" H x 25" D SS V = 96.5 L

5. LAL O/F tank

   48" H x 42" D SS V = 1090 L

6. spent tank (auto. pH)

   24" H x 15.5" D Polyethylene V = 74.2 L

7. settling drums

   185 L drums (Polypropylene)

8. repulp tank

   33" H x 17.25" D Polypropylene V = 126.4 L

9. flowmeters

   Gilmont #3, #5, (SS floats)

10. filter press

    Perrin
    Polypropylene plate and frame 12"
    8 chambers
    1" cakes

11. filter cloth

    CEZ POPR Albany C2473-1 and kraft paper

12. press pump

    Warren-Rupp Co.
    Model SA 1-A Sandpiper
    Bottom porting (flap valve)

13. wash pump

    Little Giant Pump Co.
    Model 3½-OM

14. spent pump

    March Mfg. Co., Inc.
    Model MDX-MT3
    Ryton "METL-LESS"

15. spent pump (auto. pH)

    Masterflex head No. 7018

16. water pump

    Masterflex head No. 7018

17. LAL O/F pump

    Little Giant Pump Co.
    Model 7-MD
    Ryton "MTL-LESS"

18. calcine feeder

    SYNTRON

19. LAL O/F transfer pump

    CEZ 31-624 30 amp pump

20. controls

    auto pH, pH meter, digital T^oC

REAGENTS

1. Spent

CEZ spent electrolyte was obtained from the stream to the purification plant (hot spent), since it contains the highest concentration of sulphuric acid (180-200 gpL H_2SO_4), a minimum amount of suspended MNO_2 and typical concentrations of impurities. The electrolyte was added to the main spent tank directly from a line located in the pilot plant.

2. LAL O/F

LAL O/F was collected in 185 L drums from the leach plant and sent to the pilot plant using a "bobcat". LAL O/F was then transferred by a centrifugal pump into the LAL O/F tank.

Since LAL O/F contains variable amounts of suspended solids, the tank was filled and the solution was mixed and then allowed to settle for at least 24 h. A clear solution was therefore normally pumped to the leach tank.

3. Water

Water used in all tests and for repulping was CEZ demineralized water obtained in the pilot plant from a direct line.

4. Calcine

The calcine samples employed were obtained from CEZ, Kidd Creek and two overseas zinc plants.

5. Zn Concentrate

The zinc concentrate was air-dried and then ground, using mortar, for blending with calcine when desired.

Blending of calcine and Zn concentrate was accomplished by using a cement mixer equipped with baffles and lid. Mixing time for a charge was set for 2 x 15 minute batches or 1 x 30 min. in smaller batches.

Leach Procedures

Calcine feeder was initially filled with 20 kg of calcine and run for about 10 min. before actual calibration. More than 20 kg in the feeder gave inconsistent rates of addition. Depending on the type of calcine used, different settings were used for calibration except for the vibrator which was kept at 100% capacity.

The tank was filled with LAL O/F or water to 80.4 L (level of O/F) and heating was started together with agitation (maximum rpm).

Prior to start-up, the pH of the solution in the tank was adjusted to the desired value, adding spent electrolyte. When temperature was reached and pH adjusted to desired value, LAL O/F or water was pumped into the funnel above the tank and the spent and calcine feeder were started simultaneously.

Temperature control was excellent even when feeding cold solutions. Most of the acid required was added from the main spent line, and only small amounts of acid came via the automatic pH controller, which maintained the pH at ±0.05 pH unit, using spent.

Leach slurry was discharged into the settling drums; the solids were repulped and fed to the Perrin press. Residue produced in the first hour of operation in the leach was always discarded. Similarly, material left in the tank at the end of the leach was not added to the leach slurry, and was discarded.

B. NEUTRAL LEACH TANK 3 and LAL RESIDUE

Neutral leach tank 3 and LAL residues were prepared on a continuous basis by leaching calcine in the CEZ pilot plant. Leach parameters investigated were (i) pH 1.5 or 3.0 in tank 1 of the neutral leach, and (ii) use of spent/H_2O or spent/jarosite overflow in the LAL. The pH in tank 3 of the neutral leach was 4.0 in all tests, while that in the LAL was 1.5, irrespective of the leachant solution employed in the LAL.

Process Flowsheet and Equipment

The pilot plant flowsheet employed is shown in Figure A-2, while the process equipment is described below.

1. leach tank:

12" H x 25" D SS V = 96.5 L

overflow: 10" H V = 80.4 L
¾" I.D. pipe
1" from bottom

mixer: lightnin

1/3 HP @ 1725 rpm

turbine: 4 bladed axial 6" D 45° pitch

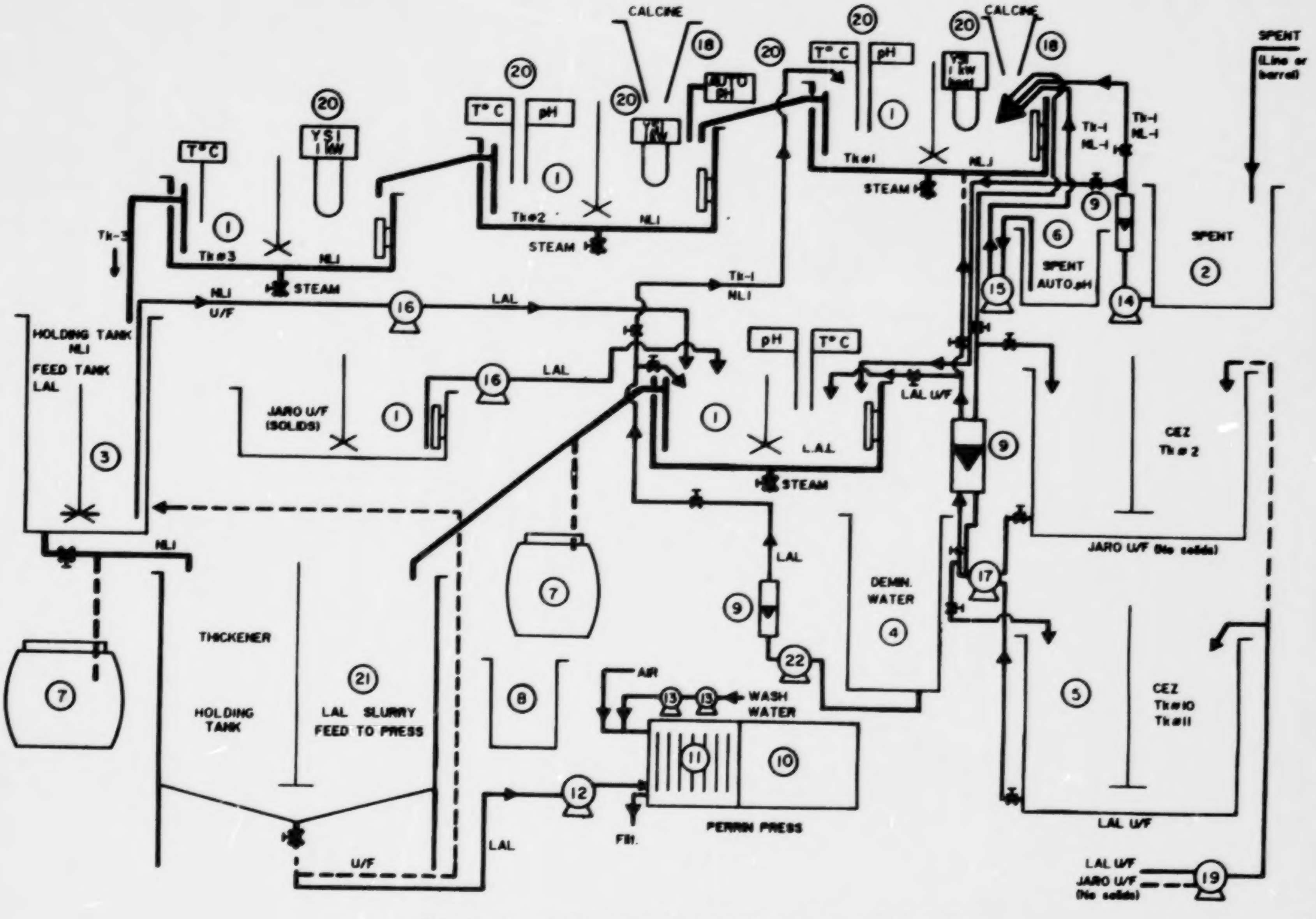
CALCINE
CALCINE
SPENT (Line or barrel)
18
18
20
20
20
20
20
20
T° C
T° C
T° C
T° C
pH
pH
pH
YSI 1 kW
YSI 1 kW
YSI 1 kW heat
AUTO pH
1
1
1
1
1
Tk#3
Tk#2
Tk#1
Tk-3
NLI
STEAM
STEAM
STEAM
STEAM
Tk-1 NL-1
Tk-1 NL-1
9
9
9
6
SPENT AUTO pH
15
14
2
SPENT
HOLDING TANK NLI
FEED TANK LAL
3
NLI U/F
16
16
LAL
LAL
Tk-1 NLI
JARO U/F (SOLIDS)
L.A.L.
LAL U/F
CEZ Tk#2
JARO U/F (No solids)
17
DEMIN. WATER
4
5
CEZ Tk#10 Tk#11
LAL U/F
LAL U/F
JARO U/F (No solids)
19
7
7
8
THICKENER
HOLDING TANK
21
LAL SLURRY FEED TO PRESS
U/F
LAL
12
22
AIR
13
13
WASH WATER
11
10
PERRIN PRESS
Filt.

Figure A-2 CEZ PILOT PLANT PROCESS FLOWSHEET

Baffles:

2" W x 10" H
½" from side
1" from bottom

Note: 3 tanks used in neutral leach 1
1 tank used for LAL
1 tank used for feed jarosite O/F (solids)

2. Spent Tank:

37" H x 18" D Polyethylene V = 154.3 L

Note: Flow directed to tank 1 NL I or LAL

3. Holding Tank:

48" H x 18" D SS V= 200.2 L

Note: Holding tank for neutral leach 1
Feed tank NL I U/F to LAL

4. Water Tank:

48" H x 18" D SS V= 200.2 L

Note: Flow directed to TK-1 NL I or LAL

5. LAL O/F Tank

48" H x 42" D SS V=1090 L

Flow directed to TK-1 NL I or LAL

6. Spent Tank (auto. pH)

24" H x 15.5" D Polyethylene V=74.2 L

Note: used to maintain constant pH in TK-1 NL I

7. Settling Drums

185 L Drums (Polyethylene)
Note: -used to collect rejected slurry from neutral leach 1 and LAL
-used to send LAL O/F and/or spent to pilot plant

8. Repulp Tank

33" H x 17.25" D Polyethylene V= 126.4 L

9. Flowmeters

Gilmont #5 (SS floats)

10. Filter Press

Perrin
Polypropylene plate and frame 12"
8 chambers
1" cakes

11. Filter Cloth

CEZ POPR Albany C2473-1 (1 cfm) and Kraft paper

12. Press Pump

Warren-Rupp Co.
Model SA 1-A Sandpiper (air operated)
Bottom porting (flap valve)

13. Wash Pump Press

Little Giant Pump Co.
Model 35-OM

14. Spent Pump

March Mfg. Co., Inc.
Model MDX-MT3
Ryton "METL-LESS"

15. Spent Pump (auto. pH)

Masterflex head No. 7018

16. NL I U/F Pump/Jarosite O/F (solids)

Masterflex head No. 7018

17. LAL O/F Pump/Jarosite O/F (no solids)

Little Giant Pump Co.
Model 7-MD (587500)
Ryton "METL-LESS"

18. Calcine Feeder

TK-1 NL I Syntron
TK-2 NL I NRC

19. LAL O/F/Jarosite O/F (no solids) Transfer Pump

CEZ 31-624 30 amp. pump

20. Controls

2 automatic pH controllers
2 digital pH meters (METROHM 632)
1 digital temperature indicator (OMEGA)
3 1000 W SS heaters
3 temperature controllers (YSl Model 63 RC)

21. Thickener

34" H x 36" D SS V = 567 L

Note: used for NL I slurry and LAL slurry

22. Water Pump

Little Giant Polypropylene 6-MD (584006)
Non submersible magnet-driven chemical pumps

REAGENTS

1. Jarosite O/F (no solids)

Jarosite O/F with a minimum amount of solids was collected from leach plant Thickener 12 in 185 L drums and sent to the pilot plant. Drums were left for 24 h settling and clear solution was then pumped to jarosite O/F tank.

2. Jarosite O/F (solids)

Jarosite O/F with solids was obtained from Thickener 12 overflow and the solids content was adjusted to 139.5 gpL solids by adding clear filtrate to jarosite pump initially containing 279 gpL of solids (18.4% solids). Jarosite slurry was then transferred to the tank.

The remaining reagents were as described above in Section A.

LEACH PROCEDURES

The calcine feeder was initially filled with 20 kg of calcine and run for about 10 min. before actual calibration. The three NL tanks were initially filled with water to 80.4 L (level of overflow) and heating was started together with agitation (maximum rpm).

Prior to start-up, the pH of the solution in tank 1 was adjusted to desired value, adding spent electrolyte. When the temperature was reached and pH adjusted to desired value, LAL O/F or water was pumped into the funnel (LAL O/F or water used for wetting calcine) and the spent and calcine feeder were started simultaneously.

Temperature control was excellent even when feeding cold solutions. Most of the acid required (spent electrolyte) was added by the main line, but additional spent electrolyte to maintain pH at ±0.05 pH unit was added by an automatic pH controller.

In tank 2, calcine was added on demand to maintain pH = 3.25 at 80°C, and this was accomplished by an automatic pH controller hooked to the calcine feeder. Temperature was maintained by using a 1000 W heater with temperature controller (YSI). In tank 3, the slurry was maintained at 80°C and there was no further calcine addition.

NL I slurry (tank 3) was discarded into a holding tank then into the thickener. Flocculant (Metritec A-321) was added and the slurry was allowed to settle. Filtrate was decanted and the thickened slurry was pumped into the holding tank which became the feed tank to the LAL. The NL U/F slurry was pumped to the LAL leach tank together with spent and jarosite O/F (no solids), jarosite O/F (139 gpL solids) or water to maintain pH = 1.5 at 85°C for 30 min. residence time. Slurry was collected in the thickener, allowed to settle, decanted, repulped with water and finally filtered on the Perrin filter press. The first hour slurry discharge from the leach was always discarded into a settling drum and discarded.

C. HIGH ACID LEACH

HAL residues were prepared by leaching LAL residue on a batch basis with spent electrolyte and water. All tests were conducted at 95°C for 6 h with 100 g/L H_2SO_4. The HAL residue was filtered and washed prior to flotation.

APPENDIX II

MINERALOGICAL EXAMINATION OF SILVER FLOTATION CONCENTRATES

Energy, Mines and Resources Canada
Énergie, Mines et Ressources Canada

CANMET
Canada Centre for Mineral and Energy Technology
Centre canadien de la technologie des minéraux et de l'énergie

MINERALOGICAL CHARACTERIZATION OF SILVER FLOTATION CONCENTRATES MADE FROM ZINC NEUTRAL LEACH RESIDUES

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Silver Recovery in the Zinc Industry

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MINERALOGICAL CHARACTERIZATION OF SILVER FLOTATION CONCENTRATES MADE FROM ZINC NEUTRAL LEACH RESIDUES

by

T.T. Chen* and J.E. Dutrizac*

ABSTRACT

Silver flotation concentrates prepared from high-silver (1,480 ppm Ag) and low-silver (300 ppm Ag) neutral leach residues have been examined mineralogically to determine the phases present and to elucidate the behaviour of silver during zinc processing. The flotation concentrates consist principally of sphalerite although lesser amounts of zinc ferrite and $PbSO_4$, as well as traces of other phases, also are present. In the high-silver flotation concentrate, silver occurs mostly as Ag_2S or $(Ag,Cu)_2S$ rims on sphalerite although $(Ag,Cu)_2S$ inclusions within sphalerite also are present. Trace amounts of a Cu-Ag-S-Cl phase are present on rare copper oxide grains, and this silver-bearing phase may be a fine mixture of Ag_2S, AgCl and Cu_2S. In the low-silver flotation concentrate, silver occurs mostly as Ag_2S although traces of silver-bearing CuS and Cu_2S also are present. The Ag_2S occurs as <1 μm particles

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*Research Scientist, Mineral Sciences Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1.

disseminated in elemental sulphur-silica gel patches, as discontinuous rims or isolated patches on sphalerite grains and as tiny free particles. Silver chloride was not detected. These studies suggest that silver dissolves during neutral leaching and subsequently reacts with sphalerite or other sulphides to form silver sulphide.

Key Words: Mineralogical characterization, silver, silver sulphide, zinc leach residues, neutral leach residues, Ag_2S rims.

INTRODUCTION

Zinc sulphide concentrates commonly contain silver in amounts ranging to 400 ppm. Despite the potential value of the contained silver, silver by-product recoveries in the zinc industry vary widely depending on the silver content of the concentrate, the process used and the presence of adjacent lead smelting facilities. Many zinc plants, even those treating concentrates with relatively high silver contents, recover no silver because of the costs and difficulties of recuperating silver from large volumes of low grade leach residue (1,2). An obvious solution to the silver recovery problem is the development of an economically viable process capable of recovering silver from either the neutral leach residue or the hot acid leach residue, and a number of such processing options already have been implemented. Flotation is a low cost method capable of yielding high recoveries together with an acceptable Ag grade. Vieille-Montagne (3) recovers ∿90% Ag and 75% Pb into two flotation concentrates prepared from hot acid leach residue. This technology is used in two V-M plants and also is practised at Metallurgie Hoboken-Overpelt's zinc refinery. Furthermore, a number of refineries recuperate silver from neutral leach residues. Mitsubishi's Akita Zinc refinery recovers about 80% of the input silver (along with some gold) by flotation with AC-404 at pH 3.5-4.0 (4). Silver is floated at the Zhuzhou smelter using acidic conditions and an unspecified black distillate as collector (5). About 70% Ag recovery into a 0.6-2.0% Ag concentrate is realized. Recent reports (6) indicate that silver flotation is being carried out at the Torreon zinc plant of MET-MEX Penoles. The high acid leach residue is processed using Teefroth A at pH 2, but few details are available.

Because of the technical and economic potential of flotation technologies to recover silver from zinc leach residues, CANMET contracted Noranda Inc. to investigate the fundamental aspects of silver flotation (7). That preliminary work indicated the potential of silver flotation from neutral leach residues, and a subsequent contract was issued to Noranda Inc. to develop neutral leach flotation technology and to define the neutral leaching parameters which yield the best silver recoveries in the subsequent flotation circuit. The flotation concentrates detailed in this report were prepared by Noranda during the course of the second contract study (8). The flotation concentrates were prepared under the identified preferred conditions, and one of the samples was generated during a prolonged locked-cycle test program. Although the Noranda work identified the preferred neutral leaching and flotation conditions and generated a large body of chemical data on the flotation concentrates, it did not address the "mineralogy" of the flotation concentrates. A number of recent studies (9), however, have demonstrated that detailed mineralogical techniques can complement chemical data by defining the phases present, illustrating their morphologies and elucidating some of the reactions which occur in the preceeding leaching operations. To provide such complementary information to the Noranda flotation contract, CANMET undertook a detailed mineralogical study of three of the flotation concentrates, and the results of those mineralogical studies are summarized in this report.

EXPERIMENTAL

Samples

Three flotation concentrates were provided for study by Noranda. All the samples were derived by flotation of a neutral leach residue generated by Noranda by the leaching of either a high-silver or a low-silver commercial calcine. The details of the leaching and flotation procedures have been outlined by Noranda (8), and some of the relevant analytical data generated by the company are presented in Table 1.

The high-silver flotation concentrate was made by leaching high-silver calcine with spent electrolyte at pH = 1.5 to generate a neutral leach residue. The residue was well washed and then was subjected to slow flotation at pH = 3.5 using 200 g/t R-3501 and 150 g/t S-4037 as flotation reagents. The rougher concentrate was subjected to two stages of cleaning as detailed in the Noranda report (8).

The low-silver flotation concentrate was prepared by leaching low-silver calcine in spent electrolyte at pH = 1.5 to generate a neutral leach residue. The neutral leach residue was well washed and

Table 1 - Analytical data provided for the three samples investigated, wt%.

Element	High-Silver Products Batch Test			Low-Silver Products Batch Test			Low-Silver Products Locked-cycle Test		
	Calcine	NL leach residue	Flotation concentrate	Calcine	NL leach residue	Flotation concentrate	Calcine	NL leach residue	Flotation concentrate
Zn	58.7	22.4	56.8	63.2	23.0	49.5	63.2	24.2	42.2
Fe	6.67	-	5.17*	9.53	38.3	14.89*	9.53	-	13.3
Ag	0.034	0.148	2.29	0.011	0.03	0.4	0.011	0.03	0.64
Pb	2.45	-	1.31*	2.45	2.29	1.87*	2.45	8.9	1.93
S_{total}	3.48	-	28.40*	2.98	2.95	24.99*	2.98	3.2	28.6
S_{SO_4}	3.04	-	0.22*	2.59	1.55	0.33*	2.59	1.7	0.4
S^{2-}	0.44	-	27.37*	0.39	1.4	22.75*	0.39	1.5	28.2
S°	-	-	0.81*	-	-	2.91*	-	-	14.9*

*CANMET analysis

then was subjected to slow flotation at pH = 3.5 using R-3501 and S-4037 collectors as noted above. The rougher concentrate was subjected to two stages of cleaning to yield the sample provided for study. In addition, a locked-cycle test also was carried out on the low-silver neutral leach residue under the flotation conditions described above. The concentrate from the sixth cycle was provided for study.

All the samples were well washed and dried by the company; all were examined in their as-received states.

Mineralogical Techniques

The three flotation concentrates were studied by both Debye-Scherrer and Guinier-deWolff X-ray diffraction analyses using filtered Co K_α radiation ($\lambda = 1.7889$ Å). Some of the fractions were analyzed with a Rigaku X-ray powder diffractometer with a rotating anode and using filtered Cu K_α radiation ($\lambda = 1.5418$ Å). Polished sections of the samples were prepared, and these were examined using ore microscopy, scanning electron microscopy (SEM) and electron microprobe analysis. The principal mineral constituents and coarse grained silver carriers were easily detectable using classical ore microscopy. Finer grained silver-containing regions in the polished sections, however, were located using the wavelength-dispersive spectrometers on the electron microprobe that are equipped with an audio detection system. These regions then were examined in detail using the SEM with an energy-dispersive X-ray analyzer (EDX). Synthetic standards such as Ag°, Pb°, Ag_2S, Ag_2SO_4, PbS and $PbSO_4$ were analyzed frequently for comparison purposes. Some of the coarser grains in the two samples also were analyzed with a JEOL 733 electron microprobe; the data were corrected using standard ZAF correction programs. Although much of the phase characterization was done using polished sections of the samples, considerable work also was done using loose powder mounts as such studies provide complementary information.

RESULTS AND DISCUSSION

HIGH-SILVER FLOTATION CONCENTRATE

General Observations

Table 1 summarizes the compositions of the high-silver neutral leach residue and the flotation concentrate prepared from this residue. The flotation concentrate contains 56.8% Zn as well as 2.3% Ag. The composition is generally consistent with sphalerite, and in fact, X-ray diffraction analysis of the as-received flotation concentrate indicated major sphalerite, minor amounts of zinc ferrite, as well as traces of other unidentifiable phases.

Detailed optical microscopy and SEM-EDX study confirmed that sphalerite was the major constituent of the flotation concentrate. Figure 1 presents a general view of the flotation concentrate as observed in polished section. Virtually all of the particles in the photomicrograph are sphalerite which is present as liberated particles from 1 to 80 μm in size. Although many of the grains have rounded edges indicative of partial dissolution, other grains still have sharp corners suggesting they have passed through the roasting and neutral leaching circuits largely unaltered. Although some of the sphalerite particles are cracked, most are compact and show little evidence of abrasion or thermal shock. SEM-EDX study of the sphalerite revealed that most of the grains contained <2% Fe in solid solution in the structure although a few iron-rich sphalerite particles were observed. As will be shown later, many of the low-iron sphalerite grains have a rim of silver sulphide or silver-copper sulphide. Although some of the high-iron sphalerite grains also have silver sulphide rims, many iron-rich sphalerite particles are rimless. Low-iron sphalerite predominates in the flotation concentrate, and this may be a consequence of the selective roasting and leaching of the high-iron particles.

Zinc ferrite was detected by X-ray diffraction analysis of the flotation concentrate and SEM-EDX study confirmed the presence of a number of zinc ferrite particles. Figure 2 illustrates a mass of porous zinc ferrite (Phase 1) on a partly roasted sphalerite grain (Phase 2). The massive ferrite probably formed by the oxidation of iron-rich sphalerite, and there seems to be a fairly sharp contact between the $ZnFe_2O_4$ and the (Zn,Fe)S. Although the porosity observed in the ferrite could be a growth feature, it equally could reflect the preferential dissolution of associated ZnO during neutral leaching. Also illustrated is a thin rim of zinc ferrite (Phase 3) on sphalerite. The rim is 1-2 μm thick, and in many places has separated from the underlying sphalerite. Presumably, the rim initially covered the entire surface of the sphalerite, but parts have broken off during subsequent handling. A number of sphalerite grains partly rimmed by $ZnFe_2O_4$ were observed. Figure 3 illustrates an irregular and very porous zinc ferrite particle (Phase 1) associated with badly fractured sphalerite (Phase 2) and a ∿10 μm silver sulphide particle (Phase 3). The zinc ferrite is compact, but its irregular shape suggests that originally associated ZnO may have been dissolved during neutral leaching. Many <4 μm fragments of zinc ferrite are evident and small $ZnFe_2O_4$ crystals were dispersed throughout the flotation concentrate. The light <2 μm patches on the surface of the ferrite are $PbSO_4$ (Phase 4), and the porous ferrite grains commonly contained $PbSO_4$ particles.

Figure 4 illustrates a rare and unusual ring-like structure 1-2 μm thick and consisting of $ZnFe_2O_4$ and Fe_2O_3 (Phase 1). The tiny light specks associated with the ring are Ag_2S or $PbSO_4$ (Phase 2) and the "core" is CuS (Phase 5). The ring-like structure is surrounded by numerous sphalerite particles (Phase 3) as well as isolated 10 μm grains of Ag_2S (Phase 4). Presumably the ferrite ring formed originally on a sphalerite or ZnO particle which has been removed in neutral leaching. It is surprising that such a fragile structure has survived the subsequent processing steps.

EDX study of the various zinc ferrite grains failed to detect any silver in the ferrite itself. A few tiny Ag_2S patches sometimes were present on the ferrite (Figure 4), but extensive silver sulphide rims never were observed.

The flotation concentrate contains some lead, and most of the lead is present as $PbSO_4$. A number of $PbSO_4$ grains were observed in the SEM-EDX studies, and some of these were <5 μm particles associated with sphalerite or zinc ferrite (Figure 3). In most instances, $PbSO_4$ occurred as free particles ranging from 2-20 μm in size. Figure 5 shows a large irregular mass of $PbSO_4$ about 20 μm across. The $PbSO_4$ is not closely associated with other phases, and this may represent material precipitated and agglomerated during neutral leaching. Barite ($BaSO_4$) also occurs in the flotation concentrate, and the barite particles invariably are rimmed by $PbSO_4$ as indeed are rare particles of Ba-Al-Zn silicate observed in the concentrate. Figure 6 shows a $\sim$50 μm barite grain (Phase 1) extensively rimmed by $PbSO_4$ (light, Phase 2). The presence of $PbSO_4$ rims on barite suggests the partial dissolution of lead sulphate in the warm neutral leach circuit and its subsequent selective precipitation on isostructural $BaSO_4$ grains during cooling. Silver was not detected in either the lead or barium sulphates.

A number of other phases, usually present in trace amounts, also occur in the high-silver flotation concentrate. Pyrite occurs both as isolated free grains and as tiny inclusions in sphalerite. Galena, pyrrhotite, chalcocite, chalcopyrite, and possibly cubanite ($CuFe_2S_3$) also are present as rare isolated inclusions in sphalerite. None of these inclusions contributes significantly to the total amount of silver and none likely influences the flotation of silver from the neutral leach residue. Covellite (CuS) is a common constituent of the rims formed on sphalerite, but the copper sulphide is invariably associated with silver sulphide and will be considered below.

Some grains of copper oxide are present, but these also are associated with silver-bearing constituents and will be reviewed below. A few porous grains of Fe_2O_3, possibly originating from the roasting of free pyrite particles, were detected in close association with zinc ferrite. The Fe_2O_3 is considerably less plentiful than zinc ferrite which itself is a minor constituent of the flotation concentrate. A few large grains of quartz, K-Al silicate and Mg-Al-Fe silicate were detected, but silicates are relatively rare in the flotation concentrate. Silica gel was not detected. One or two tiny SnS particles were observed, and this phase likely accounts for all the tin present in the concentrate. Although a few optically transparent masses of K-Fe sulphate, with minor Pb and trace Zn, were detected, jarosite-type compounds were not observed in the flotation concentrate despite their probable presence in the neutral leach residue feed to the flotation circuit.

Gold

Although zinc concentrates and zinc leach residues normally are not considered for their gold values, a significant amount of gold was detected in the high-silver silver flotation concentrate. Ten grains of gold were observed in one polished section and seven in a second polished section; these quantities suggest that the flotation product is a gold as well as a silver concentrate.

Figure 7 indicates a typical ∿20 μm gold particle (Phase 1) surrounded by sphalerite grains (Phase 2). The gold is spheroidal in shape and is compact; it is not intergrown with any other phases. Figure 8 illustrates a somewhat smaller ∿10 μm gold grain (Phase 1) which is closely associated with small zinc ferrite particles (Phase 2); it is not known whether the gold is actually attached to the ferrite grains although the ferrite grains seem to fit into shallow depressions in the gold. SEM-EDX study of the gold particles indicated traces of silver (likely <1% Ag) as the only detectable impurity. The flotation process has significantly concentrated the gold values in the original zinc calcines to the point where gold recovery should be possible.

Silver-Bearing Phases

The silver flotation concentrate made from the high-silver neutral leach residue contains 2.3% Ag. The most common occurrence of silver is as thick rims or partial rims of silver sulphide on sphalerite grains. Figure 9 illustrates a ∿20 μm sphalerite grain (Phase 1) partly rimmed by Ag_2S (light, Phase 2). The silver sulphide seems to have been formed by reaction of dissolved silver with the sphalerite, and the Ag_2S scale is tenaciously attached to the zinc mineral. SEM-EDX analysis of the silver sulphide indicated traces of Cu, Fe, Pb and sometimes Zn. The sphalerite core consists of Zn and S; it is essentially iron-free. By contrast, the adjacent sphalerite grain (Phase 3) contains ∿2% Fe, but has no silver sulphide rim. As a general observation, the low-iron sphalerites tend to be the dominant silver carriers. Figure 10 illustrates another low-iron sphalerite particle (Phase 1) rimmed by relatively thick layers of Ag_2S. The adjacent sphalerite particles contain 2-3% Fe, and all these grains remain silver-free. The silver sulphide rim illustrated in Figure 10 seems to have grown onto the sphalerite and is tenaciously attached to the zinc sulphide. It is felt that the silver in the roaster calcine occurs as Ag, Ag_2SO_4 or possibly AgCl (10). During neutral leaching, the silver is solubilized and reacts with the sphalerite:

$$2Ag^+ + ZnS \longrightarrow Ag_2S + Zn^{2+} \tag{1}$$

The silver sulphide replaces the ZnS, and, consequently, the overall particle shape does not change significantly and the Ag_2S is tenaciously adherent.

Figure 11 shows a number of sphalerite particles (Phase 1) as observed in a loose powder mount. The central grain is sphalerite, the periphery of which has been heavily coated with Ag_2S (light, Phase 2). In some cases, the Ag_2S has a crude morphological form which could be consistent with Reaction 1. In cross-section, this grain presumably would appear somewhat like the particles illustrated in Figures 9 and 10. The sphalerite particle to the left of the central grain of Figure 11 has only a few isolated patches of Ag_2S, whereas the sphalerite grain at the right is silver-free. Figure 12 shows two sphalerite particles in a loose powder mount. The grain at the right is nearly silver-free, whereas the particle at the left is extensively covered with <4 μm Ag_2S crystals (light, Phase 1). The Ag_2S crystals commonly are isolated although in a few areas they have grown into larger masses or elongated forms. Figure 13 shows the Ag_2S crystals on the sphalerite surface in more detail. The sphalerite itself is slightly etched although deep pitting is not observed. The Ag_2S grain (Phase 1) occurs as discrete crystals firmly attached to the sphalerite surface. This suggests that the deposition of silver occurs at specific sites and that the dissolution of zinc occurs from adjacent areas. In some instances, the Ag_2S crystals and leached sphalerite form a grid-like network, and one such deposit is illustrated in Figure 14. The Ag_2S phase (light, Phase 1) entirely covers the sphalerite grain. The Ag_2S and leached sphalerite form a grid-like texture which presumably allows the precipitation of Ag_2S and the simultaneous dissolution of zinc according to Reaction 1. Figure 14 also provides further evidence of the great differences in reactivity among different sphalerite particles. Although one grain is entirely covered by Ag_2S, the adjacent sphalerite grain (Phase 2) is essentially free of any silver deposit.

The silver sulphide rims described above consist mostly of Ag_2S with traces of Cu, Fe, Pb and possibly Zn. In addition to these Ag_2S coatings, rims of Ag-Cu sulphide, in which both Ag and Cu occur in significant and variable concentrations, also were detected. Figure 15 illustrates a low-iron sphalerite grain (dark, Phase 1) almost completely encapsulated by $(Ag,Cu)_2S$

(light, Phase 2). The sulphide rim ranges from 2-10 μm in thickness and in places seems to consist of two phases, one of which is Ag-rich, likely Ag_2S, and the other Cu-rich, $(Ag,Cu)_2S$. The neutral leaching operation solubilizes copper in addition to silver. It is well established that copper reacts with sphalerite to form copper sulphide, and the Ag-Cu sulphide rim of Figure 15 likely is formed by this mechanism. Reaction 1 is further supported by the fact that the original crystallographic directions (Phase 3) of the sphalerite grain are still visible in the Ag-Cu sulphide rim. It is not known if an Ag-Cu sulphide solid solution forms or whether the rim is an intimate mixture of silver sulphide and copper sulphide. The optical properties, however, suggest a single solid solution member. Figure 16 illustrates another Ag-Cu sulphide layer on sphalerite. The sphalerite (Phase 1) is extensively coated by Ag-Cu sulphide. Intensity variations within the Ag-Cu sulphide rim suggest significant differences in the Ag/Cu ratio. In particular, the darker material near the sphalerite may be $(Cu,Ag)_2S$ (Phase 2) whereas the lighter phase on the periphery is probably $(Ag,Cu)_2S$ or Ag_2S (Phase 3). Again, Reaction 1 (substitution of Zn by Ag or Cu) is supported by the presence of the original sphalerite twinning lamellae or compositional zoning (Phase 4) in the Ag-Cu sulphide layer.

Figure 17 illustrates an elongated grain, the central part of which consists of sphalerite (Phase 1) and both extremities are $(Ag,Cu)_2S$ or $(Cu,Ag)_2S$ (Phase 2). Although these extensive Ag-Cu sulphide regions also may be due to silver and copper replacement of sphalerite, they equally could represent composite ZnS-Cu_2S particles in the calcine that have reacted with dissolved silver to form $(Ag,Cu)_2S$ from Cu_2S. The darker "cores" of the grain possibly suggest the original existence of copper sulphide, but it is not known whether the copper sulphide existed in the calcine or whether it formed during neutral leaching. There is considerable intermixing of the Ag-rich (lighter) and Cu-rich (darker) phases, and this also suggests a reaction between originally-formed Cu_2S and dissolved silver:

$$Cu_2S + Ag^+ \longrightarrow Cu^+ + (Cu,Ag)_2S \qquad (2)$$

$$(Cu,Ag)_2S + Ag^+ \longrightarrow Cu^+ + Ag_2S \qquad (3)$$

Presumably Reactions 2 and 3 occur at active sites on the copper sulphide, and this leads to the somewhat irregular silver-rich areas noted in Figures 16 and 17.

In addition to various Ag_2S and $(Ag,Cu)_2S$ rims, silver-copper sulphides also were observed within individual sphalerite grains. Figure 15, for example, illustrates several inclusions of $(Ag,Cu)_2S$ in sphalerite. In some instances, spheriodal inclusions exist although in other cases the $(Ag,Cu)_2S$ seems to be spread along cracks in the sphalerite. Figure 18 illustrates a ∿40 μm sphalerite grain with numerous ribbon-like inclusions of $(Ag,Cu)_2S$ (light) and $(Cu,Ag)_2S$ (grey) dispersed throughout the sphalerite. Although some of the particles may have formed along cracks, many of the "ribbons" seem to occur in compact sphalerite. The belief is that such Ag-bearing inclusions form by the reaction of dissolved silver with pre-existing Cu_2S inclusions. In this regard, Figure 19 illustrates a sphalerite grain (Phase 1) containing numerous globular and elongated inclusions. Most of these inclusions consist of Cu_2S essentially free of silver (dark, Phase 2). Other inclusions, especially those in contact with the surface, are silver-bearing and some are $(Ag,Cu)_2S$ (light, Phase 4). Some of the elongated inclusions suggest a gradual replacement of Cu_2S by silver to form $(Ag,Cu)_2S$ within individual sphalerite particles. In extreme cases, nearly complete removal of the originally present copper is effected, and the result is an Ag_2S inclusion (Phase 3) within the sphalerite. Figure 20 shows one such Ag_2S inclusion (Phase 1) within a large sphalerite grain (Phase 2). The buried inclusion seems to be connected to the surface by a series of thin voids and cracks which may have allowed solution access to the interior of the sphalerite.

Many of the sphalerite grains have a thin rim of CuS which likely forms by the reaction of solubilized copper with residual sphalerite:

$$Cu^{2+} + ZnS \longrightarrow Zn^{2+} + CuS \qquad (4)$$

Although such copper sulphide rims could be produced during the flotation operation, the CuS rims present in the flotation concentrate commonly contain a few percent Ag, and this suggests that the rims likely formed during neutral leaching. The Ag-bearing CuS rims on sphalerite are a minor silver carrier in this flotation concentrate.

Careful SEM-EDX study of the flotation concentrate revealed a number of copper oxide grains (Cu_2O?) to 100 µm in size; Figure 21 illustrates one such copper oxide particle. The copper oxide particles consistently are rimmed with a somewhat porous layer containing Cu, Ag, S and Cl. The rim is clearly multiphase, but the individual particles are too small to provide a positive identification. The belief, however, is that the rim consists of finely mixed Ag_2S, Cu_2S and AgCl. The complex rims on the copper oxide particles are comparatively rare, and hence, they are only a trace silver contributor. These rims, however, are the only occurrence of AgCl in the high-silver flotation concentrate. Careful searches for discrete AgCl particles were carried out, but no AgCl was detected.

LOW-SILVER FLOTATION CONCENTRATE

General Observations

Table 1 summarizes the compositions of the two flotation concentrates made from the low-silver neutral leach residue. The two low-silver neutral leach residues are very similar and result in flotation concentrates which differ only slightly in composition. The concentrate prepared from the locked-cycle test is lower in zinc and richer in elemental sulphur, but contains 0.64% Ag as compared to the 0.4% Ag content of the concentrate made in the batch test. Both compositions are indicative of sphalerite, and in fact, X-ray diffraction analysis indicated sphalerite to be the major constituent of both concentrates. Minor amounts of zinc ferrite and of elemental sulphur also were detected by X-ray diffraction analysis of the as-received flotation concentrates.

Figure 22 presents a general view of the low-silver flotation concentrate prepared in the locked-cycle test. The concentrate prepared in the batch test has a similar composition and morphology. As expected from the analytical data of Table 1, sphalerite is the major phase, and the sphalerite is present as grains ranging from 1 to 100 μm in size. Semi-quantitative SEM-EDX analysis indicated the iron content of the various sphalerite grains to be 0-4%, and this range is lower than that of the sphalerite in the original concentrate processed. Although several of the larger particles show evidence of pitting or localized leaching, many of the smaller grains are compact and retain their original angular habit. Most of the larger sphalerite particles are rimmed with a thin layer of zinc ferrite, $ZnFe_2O_4$, and several porous masses of zinc ferrite also are present. Figure 23 illustrates in more detail the ferrite rim on a pitted sphalerite grain containing ∿1% Fe. The ferrite rim is compact and about 1 μm thick. The rimming of the sphalerite grain is incomplete, and this suggests that part of the rim has been removed by abrasion during the neutral leaching and flotation operations. Figure 24 illustrates the flotation concentrate made in the batch flotation test and as seen in a loose powder mount. Although some of the sphalerite grains are free of any coating, most of those illustrated have a thin rim of zinc ferrite with a fine granular texture. Discrete crystals of zinc ferrite, 0-10 μm in size, are present in both low-silver flotation concentrates, and Figure 25 illustrates several such blocky $ZnFe_2O_4$ crystals associated with large sphalerite grains in the locked-cycle low-silver flotation concentrate.

Table 1 indicates that the low-silver concentrates contain ∿2% Pb, and most of this lead is present as <2 μm free grains. Figure 26 illustrates several tiny $PbSO_4$ grains (bright) associated with sphalerite or elemental sulphur. The $PbSO_4$ particles represent either fully oxidized tiny galena grains or rims broken from larger galena particles. Although $PbSO_4$ is the dominant lead carrier, a few 10-15 μm galena grains completely rimmed by a ∿1 μm $PbSO_4$ layer also were detected, and the galena cores may be a very minor silver carrier in the concentrate. Figure 26 also contains a ∿4 μm nebulous mass of elemental sulphur, and many such sulphur particles were observed. In addition to the tiny masses of sulphur, elemental sulphur coatings on sphalerite grains also were present, and Figure 27 shows one such particle. The elemental sulphur layer is only a few microns thick and likely originates by the superficial ferric sulphate attack of the sphalerite in the more acid parts of the neutral leach circuit. The presence of an elemental sulphur film certainly would promote the flotation of the sphalerite.

A small amount of CuS is present as fine free particles or as rims on sphalerite, and the CuS phase usually contains minor amounts of silver; also, a few tiny inclusions of Cu_2S are present in sphalerite. The low-silver flotation concentrates also contain traces of quartz, silicates, Fe_2O_3, an iron-zinc sulphate, pyrite and SnO_2. Aside from the copper sulphides, none of the trace constituents likely affects the deportment of silver during the flotation operation. Two grains of gold were observed in the locked-cycle concentrate, and the flotation of even this small amount of gold may be of commercial significance.

Silver-Bearing Phases

In the high-silver flotation concentrate discussed above, the principal silver occurrence is thick Ag_2S rims on sphalerite. Although some Ag_2S rims on sphalerite also are observed in the low-silver flotation concentrates, they are considerably less common and the rims are not as extensively developed. Figure 28 illustrates a 10 μm sphalerite particle partly rimmed by Ag_2S (bright) as observed in the locked-cycle test concentrate. The silver sulphide seems to have formed by the replacement of the sphalerite and is not simply precipitated onto the surface of the sphalerite particle. The rimming occurs in just a few areas, and nowhere is the Ag_2S layer thicker than 1 μm. As was commonly the case in the high-silver concentrate, the rimmed sphalerite grain is low-iron; semi-quantitative SEM-EDX analysis suggested an iron content of $\sim$0.5% Fe. Figure 29a shows another sphalerite particle, present in the low-silver batch flotation concentrate, which also exhibits a thin discontinuous Ag_2S rim. Figure 29b is the Ag Lα X-ray map showing the distribution of silver on this sphalerite grain. It is clear that the silver rim is concentrated in a few areas, especially in the voids in the sphalerite.. The type of rimming illustrated in Figures 28 and 29a suggests the systematic displacement of zinc from the sphalerite structure by silver, and in a process which essentially results in a partial pseudomorph of the sphalerite grain by Ag_2S.

$$2Ag^+ + ZnS \longrightarrow Ag_2S + Zn^{2+} \qquad (5)$$

In loose powder mounts, the Ag_2S rims on sphalerite appear as a nebulous coating as can be seen from Figure 30. In this instance, a ∿10 μm sphalerite grain (Phase 1) in the locked-cycle flotation concentrate is partly rimmed by Ag_2S (Phase 2). The Ag_2S rim occurs only on one side of the sphalerite grain and it appears to be ∿1 μm thick. In this instance, there seems to be a sharp discontinuity between the sphalerite and the Ag_2S rim that may indicate that this rim has formed by precipitation of the Ag_2S onto the surface of the sphalerite rather than by the gradual replacement of the sphalerite by Ag_2S. Part of the large grain associated with the sphalerite seems to be Zn-Fe sulphate (Phase 3) although efforts were not made to characterize this phase further. The sulphate likely is crystallized leach solution.

In addition to occurring as discontinuous rims on sphalerite, silver also is present as isolated grains or as masses of individual particles on sphalerite. The sphalerite grain illustrated in Figure 31 is ∿20 μm in size and has been extensively pitted during the neutral leaching operation. This particular grain was collected in the batch flotation test, but similar particles were identified in both low-silver flotation concentrates. A number of <1 μm grains of Ag_2S are present at various sites on the surface, and presumably these have formed at active sites produced during neutral leaching. In many instances, the Ag_2S grains are ∿0.1 μm in size, and the possibility of even finer, nearly invisible, Ag_2S grains also exist. Figure 32a shows a cluster of Ag_2S particles present on a corroded sphalerite particle present in the batch flotation concentrate. The individual Ag_2S grains are <1 μm but collectively they have formed a porous, nebulous mass ∿10 μm long on the sphalerite surface. The general distribution of silver in this mass is indicated in Figure 32b. Silver is diffusely present, and this is an additional indication that the mass is composed of numerous tiny individual grains of Ag_2S. The type of morphology indicated in Figure 32 strongly suggests that the Ag_2S has simply precipitated from solution and onto the surface of the sphalerite grain. Although the mechanism of this precipitation reaction is not known, it could involve sulphide ion liberated by localized acid attack of the sphalerite.

$$ZnS + 2H^+ \longrightarrow Zn^{2+} + H_2S \qquad (6)$$

$$H_2S + 2Ag^+ \longrightarrow Ag_2S + 2H^+ \qquad (7)$$

Small amounts of acid could be trapped in pores in the sphalerite in the neutral leaching circuit, and retained there long enough to generate enough dissolved H_2S to precipitate the silver. Alternatively, the precipitation could occur by Reaction 5.

In addition to Ag_2S rims and precipitates on sphalerite, Ag_2S also occurs as discrete particles not associated with sphalerite. Figure 33 shows a $\sim$10 μm grain of Ag_2S present in the locked-cycle concentrate. The Ag_2S grain is compact, and does not seem to be attached to any other phase although it is associated with tiny particles of sphalerite and $ZnFe_2O_4$. This particular grain of Ag_2S may represent the complete replacement of an original sphalerite grain according to Reaction 5. Figure 34 illustrates the more typical morphology of "free" Ag_2S. The Ag_2S particle is $\sim$4 μm long and seems to be composed of three distinct Ag_2S grains. The grains show a modest level of porosity that may reflect a precipitation mechanism. Several particles similar to that of Figure 34 were detected in the low-silver flotation concentrates.

Despite the presence of a number of Ag_2S grains and Ag_2S rims or precipitates on sphalerite, the major occurrence of silver in the low-silver concentrates seems to be tiny Ag_2S inclusions in elemental sulphur and/or silica gel. Figure 35a shows a $\sim$15 μm mass of elemental sulphur-silica gel associated with sphalerite and zinc ferrite. SEM-EDX analysis of the sulphur-silica gel mass consistently indicated S, Zn, Fe, Ag and Si as well as occasional traces of Pb. The belief is that the Zn and Fe arise from associated or finely dispersed sphalerite or zinc ferrite grains; the lead is thought to originate from tiny $PbSO_4$ inclusions (e.g., Phase 4). The absence of discrete silicate minerals and the ubiquitous presence of Si in the sulphur strongly suggest the presence of silica gel. Silver is detected in trace to minor amounts throughout the mass of sulphur, and Figure 35b indicates both the diffuse nature and low concentration of silver present. Examination of the sulphur-silica gel mass at very high magnification (Figure 36) indicated the presence of $<0.3\ \mu m$ inclusions of Ag_2S. The inclusions are scattered throughout the sulphur-silica gel, and are without apparent external crystal form. It is not known whether the silver has precipitated on the elemental sulphur or whether the sulphur-silica gel simply has collected the fine Ag_2S grains present in the neutral leach slurry. Given the number of the Ag_2S inclusions and the low overall Ag concentration of the sulphur-silica gel masses, it is likely that all the silver in these masses occurs as Ag_2S. Significantly, chloride was not detected in the sulphur-silica gel masses. Figure 37 illustrates another mass of elemental sulphur-silica gel which also occludes several tiny sphalerite particles. SEM-EDX consistently indicated minor amounts of Ag and Si throughout this $\sim 15\ \mu m$ mass, and again, the belief is that the Si is present as silica gel and that the silver originates from $<0.3\ \mu m$ Ag_2S particles disseminated throughout the mass.

In loose powder mounts, the sulphur-silica gel phase clearly is present as structureless masses cementing together various fine particles in the concentrate. Figure 38 illustrates one such mass which is rich in silica gel. The silicon concentration of the sulphur-silica gel masses varies considerably; in some instances, silicon is present only as a trace constituent whereas in other masses, silicon is sufficiently concentrated that the particle could be viewed as a mass of silica gel containing sulphur. In all instances, however, the masses are silver-bearing, and the evidence suggests that the silver is due to tiny grains of Ag_2S dispersed throughout the sulphur-silica gel. The excellent flotation properties of the elemental sulphur likely assist the flotation of the fine grained Ag_2S. Although elemental sulphur is only a minor constituent of the low-silver flotation concentrate (Table 1), it seems to be a major silver carrier in these products.

Zinc concentrates commonly contain copper, and part of the copper dissolves during neutral leaching. In the presence of either sphalerite or soluble sulphide ion, copper is readily precipitated as CuS.

$$Cu^{2+} + ZnS \longrightarrow CuS + Zn^{2+} \quad (8)$$

$$Cu^{2+} + S^{=} \longrightarrow CuS \quad (9)$$

A number of precipitated CuS grains were detected in the low-silver flotation concentrates, and all such grains contain minor amounts of silver. Figure 39 illustrates a 2-3 μm precipitated mass of CuS that contains minor silver as estimated by SEM-EDX analysis. Although the CuS particles are silver-bearing, CuS is a relatively rare constituent of the flotation concentrates, and as a result, CuS is only a minor overall silver carrier.

A few of the larger sphalerite grains were found to contain tiny inclusions of $(Cu,Ag)_2S$, and Figure 40 illustrates several such inclusions which are <5 μm in size. Although the inclusions have significant silver concentrations as determined by SEM-EDX analysis, the belief is that the inclusions in the original concentrate consisted of only Cu_2S. That is, the silver enrichment occurred in the neutral leaching operation by the reaction of the Cu_2S with dissolved silver.

$$xAg^+ + Cu_2S \longrightarrow (Cu_{2-x}Ag_x)S + xCu^+ \qquad (10)$$

The $(Cu,Ag)_2S$ inclusions are rare in both low-silver flotation concentrates, and as a result, the silver-bearing copper sulphide inclusions are only a minor overall silver carrier.

CONCLUSIONS

A detailed mineralogical study of three silver flotation concentrates prepared from zinc neutral leach residues has been carried out. The mineralogical studies identified the phases present, illustrated their morphologies, determined the principal silver carriers and helped to elucidate the complex reactions occurring during neutral leaching.

The flotation concentrate made from the high-silver neutral leach residue consists principally of sphalerite as free grains to 80 μm; the majority of the sphalerite grains contain <2% Fe in solid solution in the sphalerite structure. Also present are minor amounts of zinc ferrite and $PbSO_4$; the ferrite occurs principally as euhedral crystals or crystal aggregates whereas the $PbSO_4$ usually is present as irregular grains <5 μm in size although $PbSO_4$ rims on barite also were detected. Traces of pyrite, galena, pyrrhotite, chalcocite, chalcopyrite, covellite, Fe_2O_3, SnS, K-Fe sulphate, quartz and silicates are present, but most of these phases are silver-free and do not affect the flotation process. Significant amounts of gold, as free 10-20 μm spheroidal grains, were detected, and the implication is that gold values are of economic significance. Silver occurs mostly as Ag_2S or $(Ag,Cu)_2S$ rims on sphalerite although $(Ag,Cu)_2S$ inclusions within sphalerite also are present. Some of the sphalerite grains are rimmed with CuS and the CuS precipitates commonly contain a few percent silver. Trace amounts of a Cu-Ag-S-Cl phase on rare copper oxide grains were detected, but this silver-bearing phase may be a fine mixture of Ag_2S, AgCl and Cu_2S.

The two flotation concentrates made from the low-silver neutral leach residue consist mostly of sphalerite as free grains to 100 μm. A minor amount of zinc ferrite is present as rims on sphalerite and as distinct crystals or crystal aggregates. A small amount of $PbSO_4$ is present as <2 μm free grains, and elemental sulphur occurs as nebulous masses associated with silica gel. Trace amounts of CuS, Cu_2S, quartz, silicates, Fe_2O_3, an iron-zinc sulphate, pyrite and SnO_2 also were detected. Two grains of gold were observed. Silver occurs exclusively as the sulphide, and a number of sulphide morphologies were present. The major silver occurrence is <1 μm Ag_2S grains dispersed in elemental sulphur-silica gel masses or slightly larger free grains of Ag_2S in the concentrates. Silver sulphide rims on sphalerite were present, but the rimming was both thin and discontinuous. In many instances, the Ag_2S appears to have precipitated onto the surface of the sphalerite. Silver-bearing CuS precipitates and Cu_2S inclusions in sphalerite are present, but both copper sulphides are minor overall silver carriers.

Silver sulphide is the dominant silver carrier in both the high-silver and low-silver flotation concentrates. The mineralogical evidence suggests the silver has precipitated from solution, and the implication is that silver dissolves during neutral leaching and subsequently reacts with sphalerite or other sulphides to form silver sulphide or silver-copper sulphide. The general absence of AgCl is notable, and likely is a reflection of the greater stability and low solubility of Ag_2S in neutral leaching solutions.

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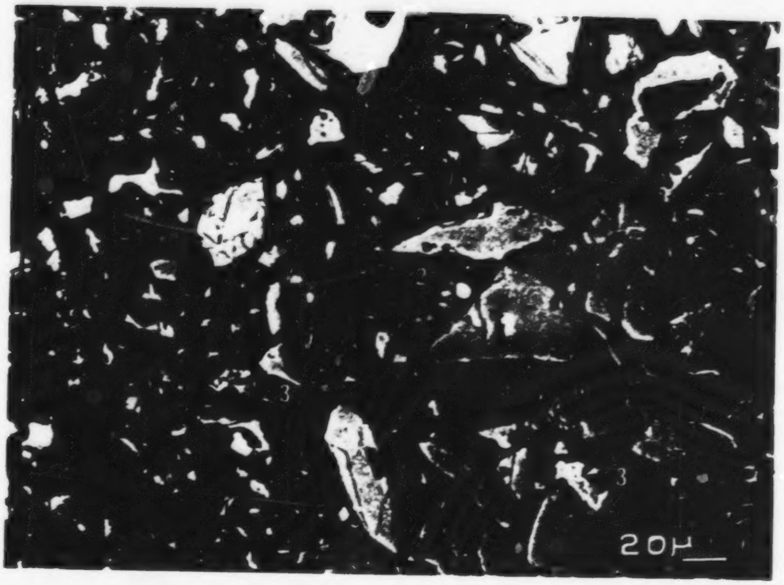

Fig. 1 - Backscattered electron micrograph illustrating the general texture of the high-silver flotation concentrate (polished section mount). 1 - sphalerite, 2 - Au, 3 - Ag_2S rim on sphalerite.

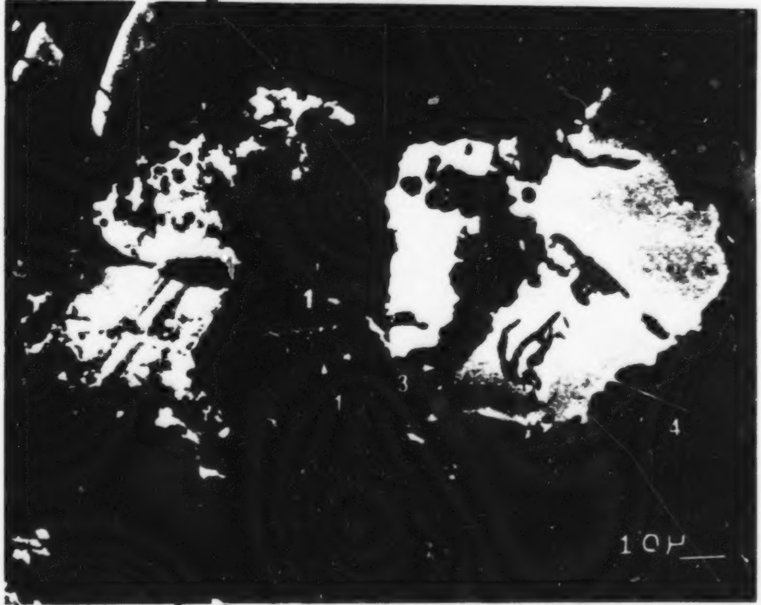

Fig. 2 - Backscattered electron micrograph of a zinc ferrite rim forming on sphalerite (polished section mount). 1 - porous $ZnFe_2O_4$, 2 - sphalerite, 3 - rim of $ZnFe_2O_4$, 4 - $(Cu,Ag)_2S$.

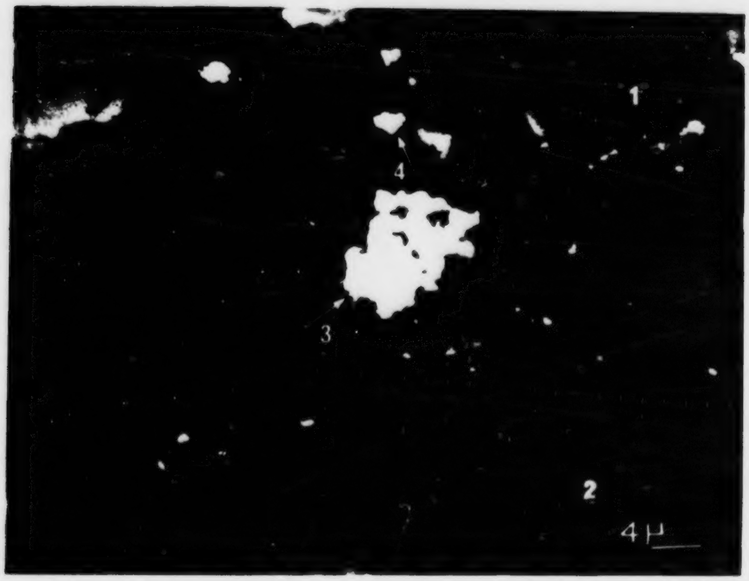

Fig. 3 - Backscattered electron micrograph of a zinc ferrite particle in the high-silver flotation concentrate (polished section mount). 1 - $ZnFe_2O_4$, 2 - sphalerite, 3 - Ag_2S, 4 - $PbSO_4$.

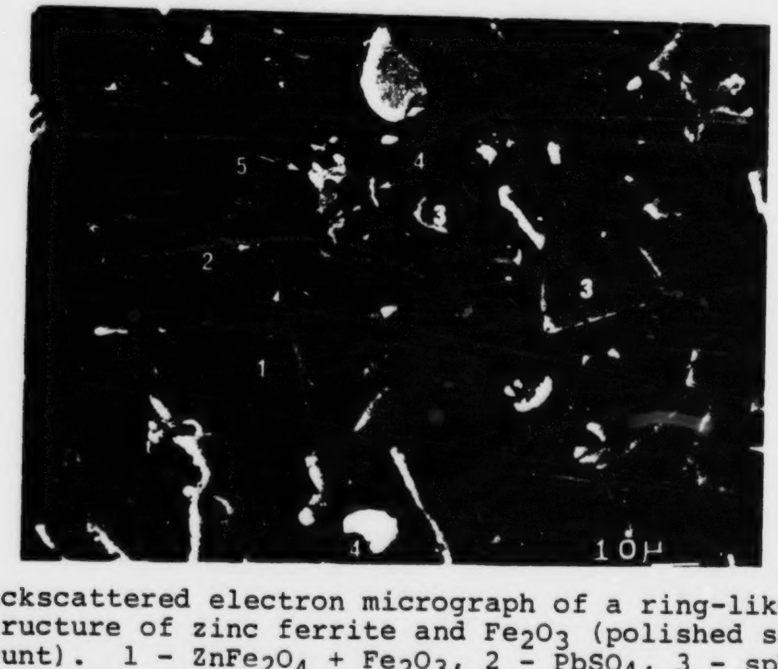

Fig. 4 - Backscattered electron micrograph of a ring-like structure of zinc ferrite and Fe_2O_3 (polished section mount). 1 - $ZnFe_2O_4$ + Fe_2O_3, 2 - $PbSO_4$, 3 - sphalerite, 4 - Ag_2S, 5 - CuS.

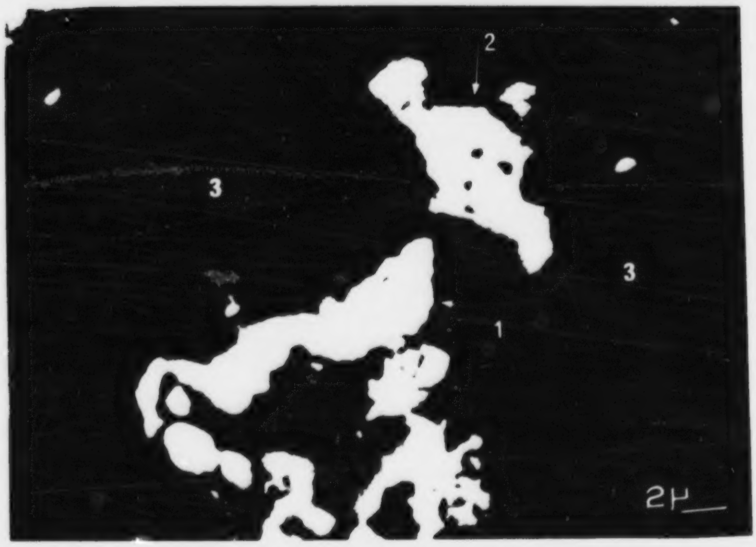

Fig. 5 - Backscattered electron micrograph of a large $PbSO_4$ particle in the high-silver flotation concentrate (polished section mount). 1 - $PbSO_4$, 2 - Ag_2S, 3 - sphalerite.

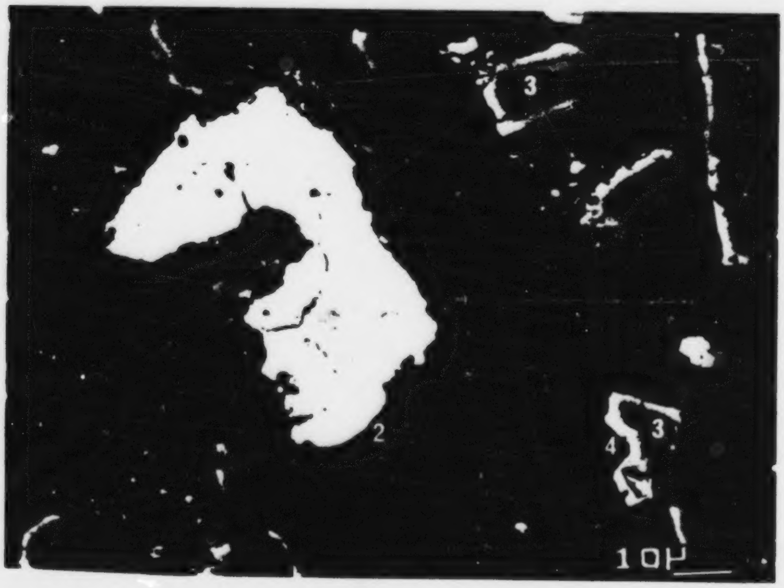

Fig. 6 - Backscattered electron micrograph illustrating $PbSO_4$ rims on barite (polished section mount). 1 - barite, 2 - $PbSO_4$, 3 - sphalerite, 4 - Ag_2S rim on sphalerite.

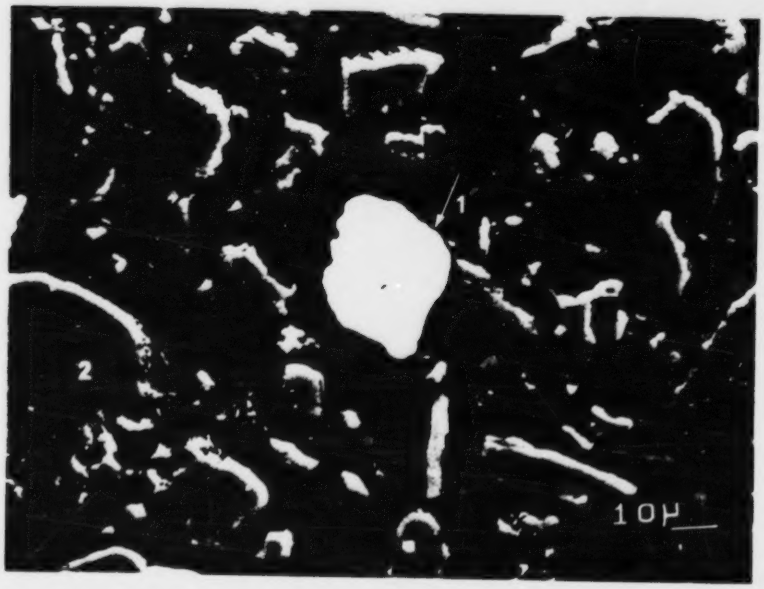

Fig. 7 - Backscattered electron micrograph of a ~20 μm gold particle in the high-silver flotation concentrate (polished section mount). 1 - gold, 2 - sphalerite.

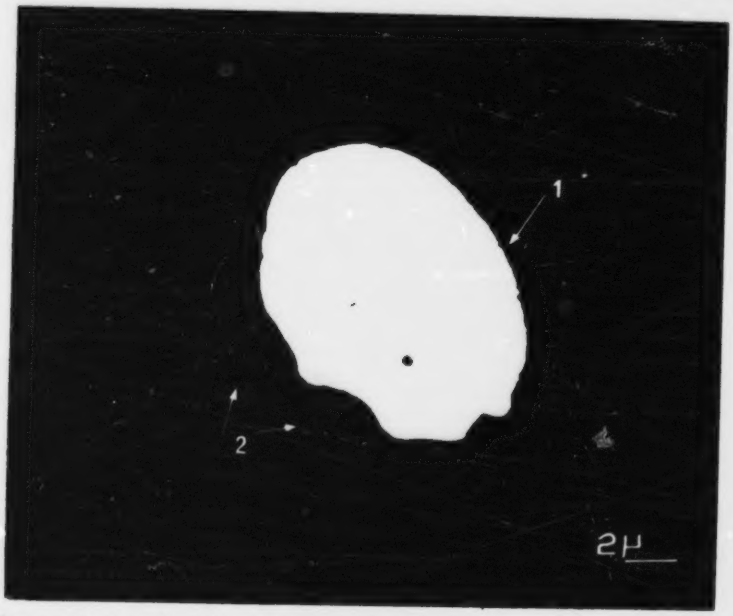

Fig. 8 - Backscattered electron micrograph of a gold grain in the high-silver flotation concentrate (polished section mount). 1 - gold, 2 - $ZnFe_2O_4$.

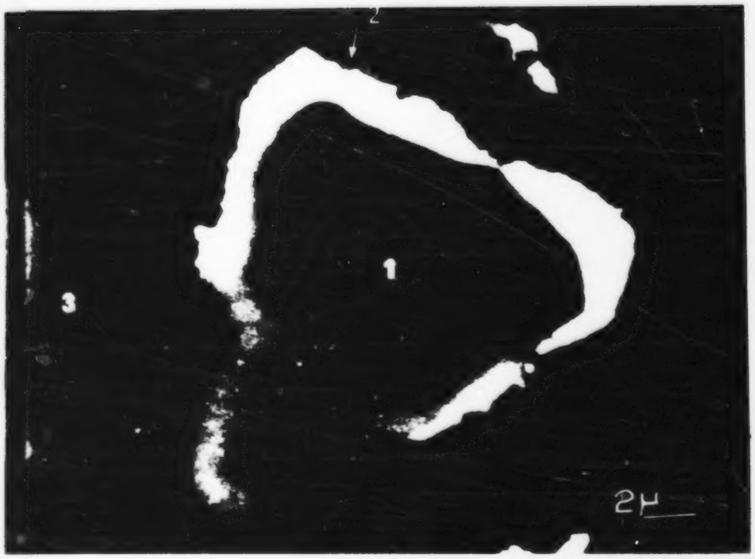

Fig. 9 - Backscattered electron micrograph of a sphalerite grain rimmed by silver sulphide (polished section mount). 1 - low-Fe sphalerite, 2 - Ag_2S rim, 3 - high-Fe sphalerite (∿2% Fe).

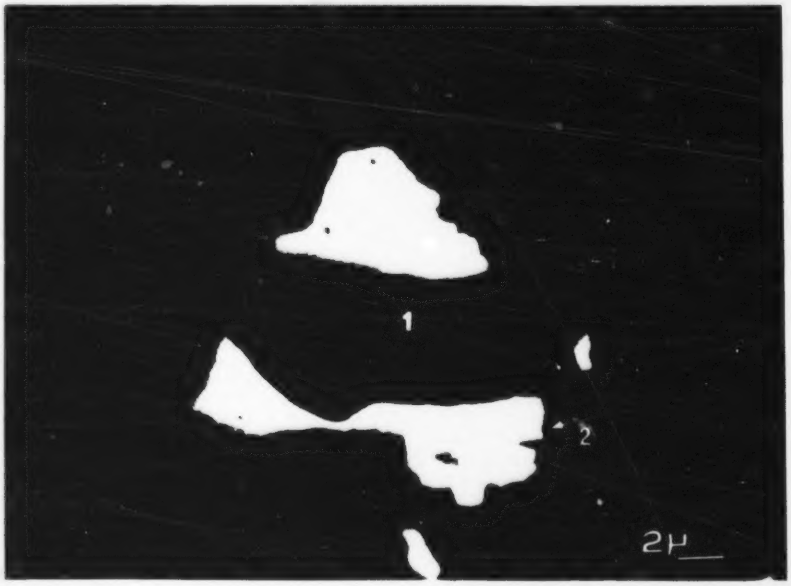

Fig. 10 - Backscattered electron micrograph illustrating a thick Ag_2S rim on sphalerite (polished section mount). 1 - low-Fe sphalerite, 2 - Ag_2S rim.

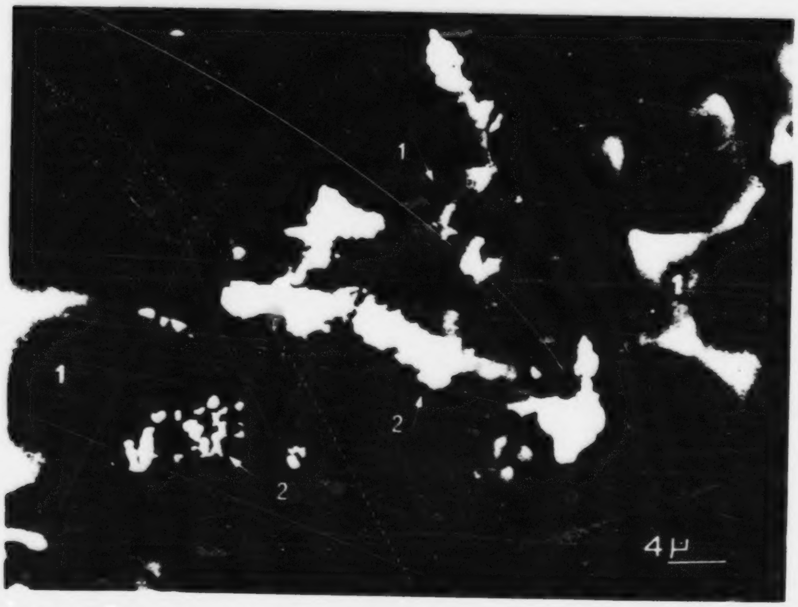

Fig. 11 - Backscattered electron micrograph of three sphalerite grains as seen in a loose powder mount. 1 - sphalerite, 2 - Ag_2S.

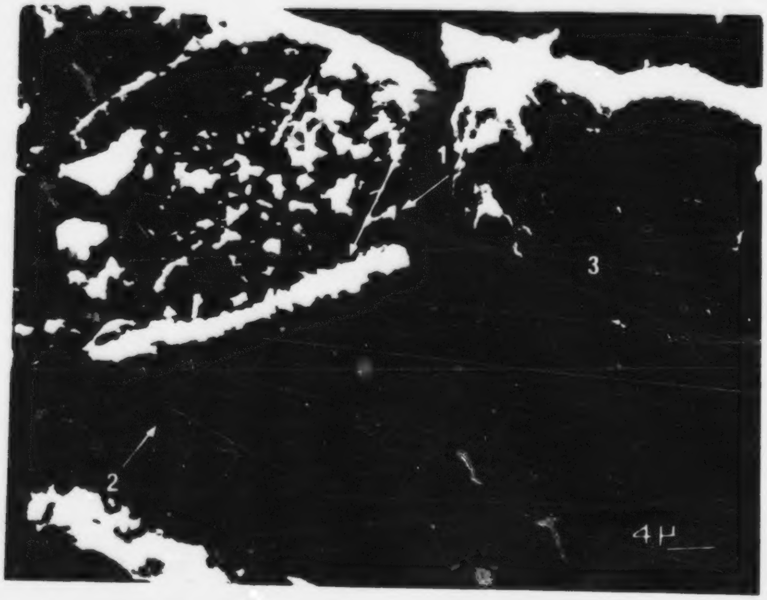

Fig. 12 - Secondary electron micrograph of two sphalerite grains, only one of which has an Ag_2S coating (loose powder mount). 1 - Ag_2S, 2 - sphalerite (matrix), 3 - sphalerite.

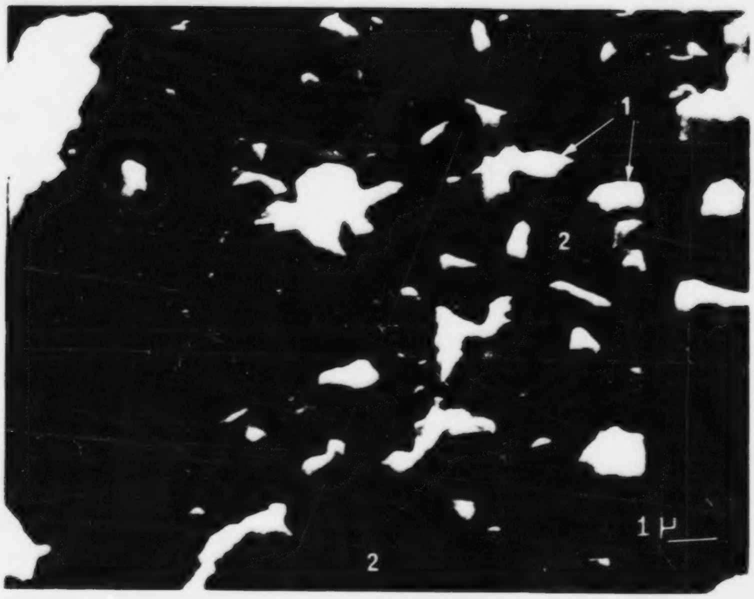

Fig. 13 - Secondary electron micrograph showing the detailed structure of the Ag_2S grains illustrated in Figure 12 (loose powder mount). 1 - Ag_2S crystals, 2 - sphalerite (matrix).

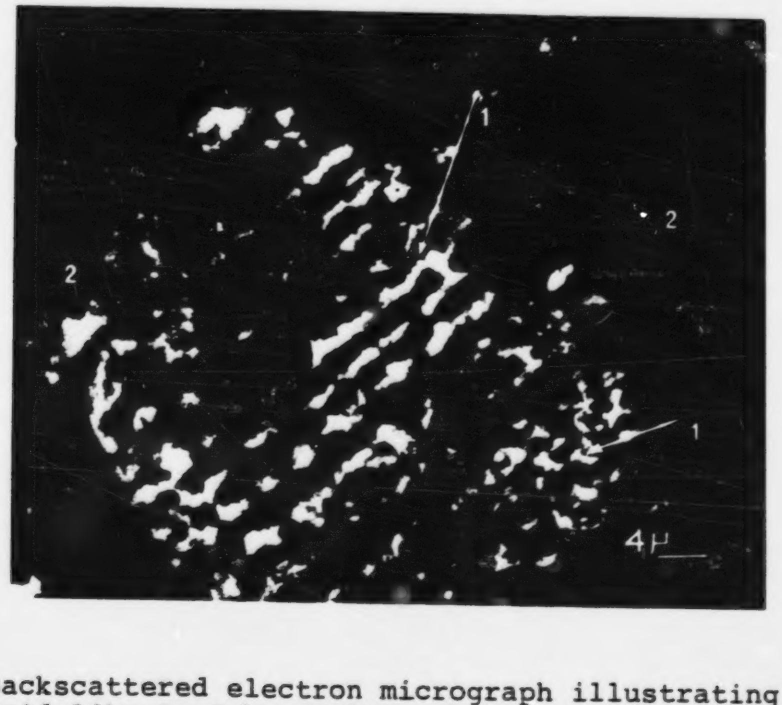

Fig. 14 - Backscattered electron micrograph illustrating a grid-like Ag_2S-leached sphalerite texture (loose powder mount). 1 - Ag_2S, 2 - sphalerite.

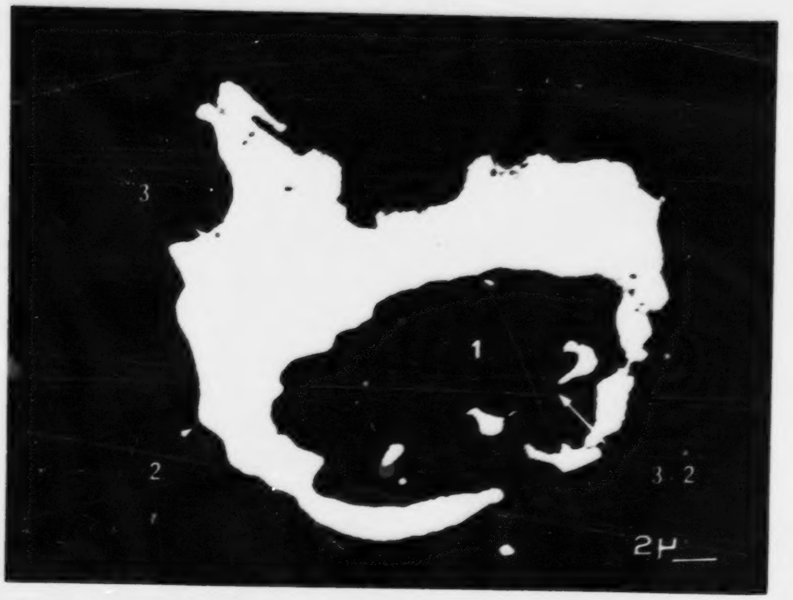

Fig. 15 - Backscattered electron micrograph of a sphalerite grain rimmed by $(Ag,Cu)_2S$ and containing $(Ag,Cu)_2S$ inclusions (polished section mount). 1 - sphalerite, 2 - $(Ag,Cu)_2S$, 3 - original crystallographic directions of the sphalerite grain.

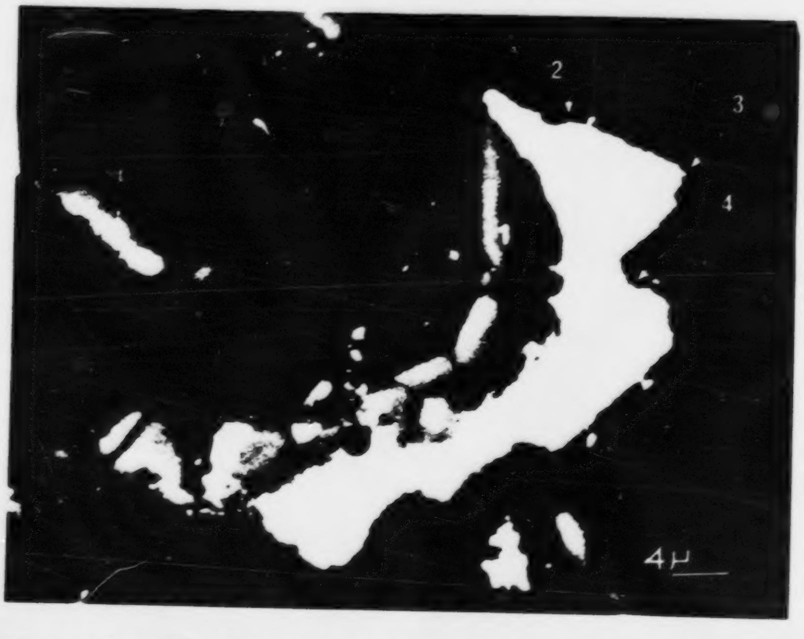

Fig. 16 - Backscattered electron micrograph of a sphalerite grain rimmed by $(Cu,Ag)_2S$ which itself is rimmed by $(Ag,Cu)_2S$ (polished section mount). 1 - sphalerite, 2 - $(Cu,Ag)_2S$, 3 - $(Ag,Cu)_2S$, 4 - original twinning lamellae or compositional zoning in sphalerite.

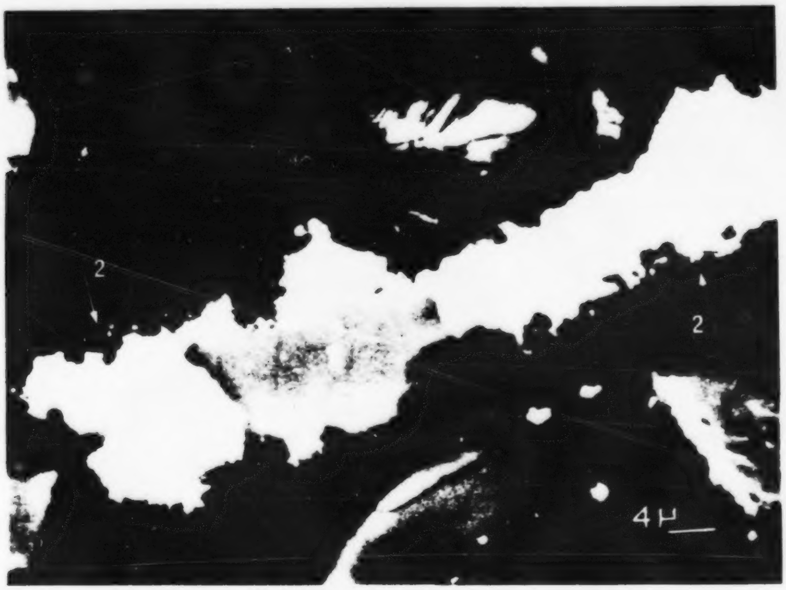

Fig. 17 - Backscattered electron micrograph of an elongated grain with a central part of sphalerite and ends of $(Ag,Cu)_2S$ or $(Cu,Ag)_2S$ (polished section mount). 1 - sphalerite, 2 - $(Ag,Cu)_2S$ (light) or $(Cu,Ag)_2S$ (dark).

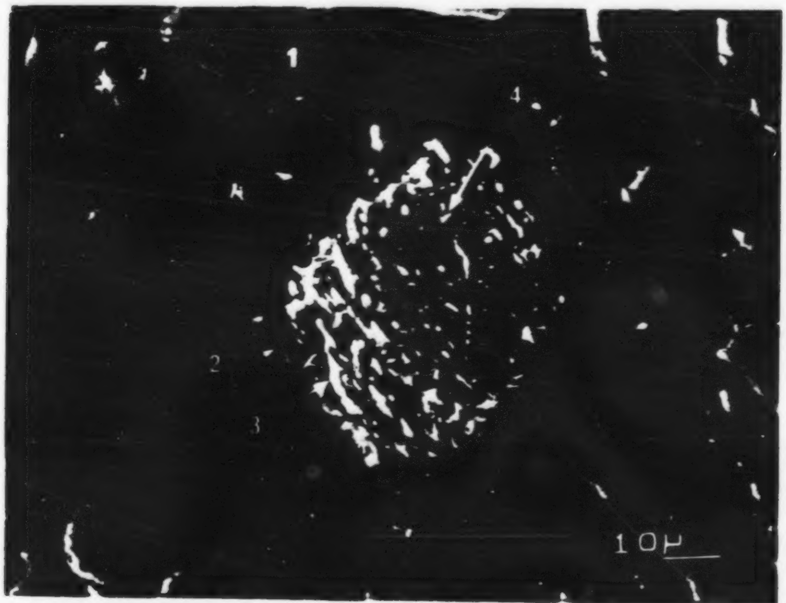

Fig. 18 - Backscattered electron micrograph of a sphalerite grain permeated with $(Ag,Cu)_2S$ and $(Cu,Ag)_2S$ inclusions (polished section mount). 1 - sphalerite, 2 - sphalerite (matrix), 3 - $(Ag,Cu)_2S$ (light), 4 - $(Cu,Ag)_2S$ (grey).

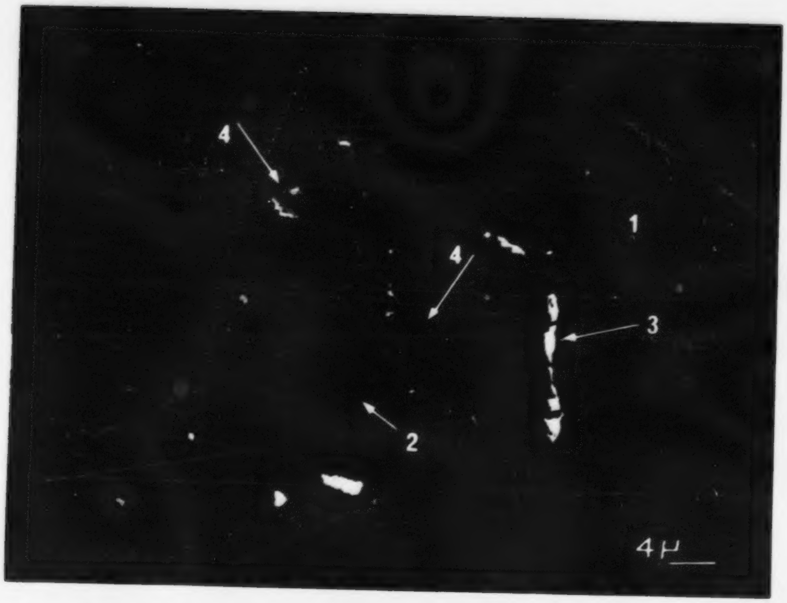

Fig. 19 - Backscattered electron micrograph of a sphalerite particle containing Cu_2S and Ag_2S inclusions (polished section mount). 1 - sphalerite, 2 - Cu_2S, 3 - Ag_2S, 4 - Cu_2S + $(Ag,Cu)_2S$.

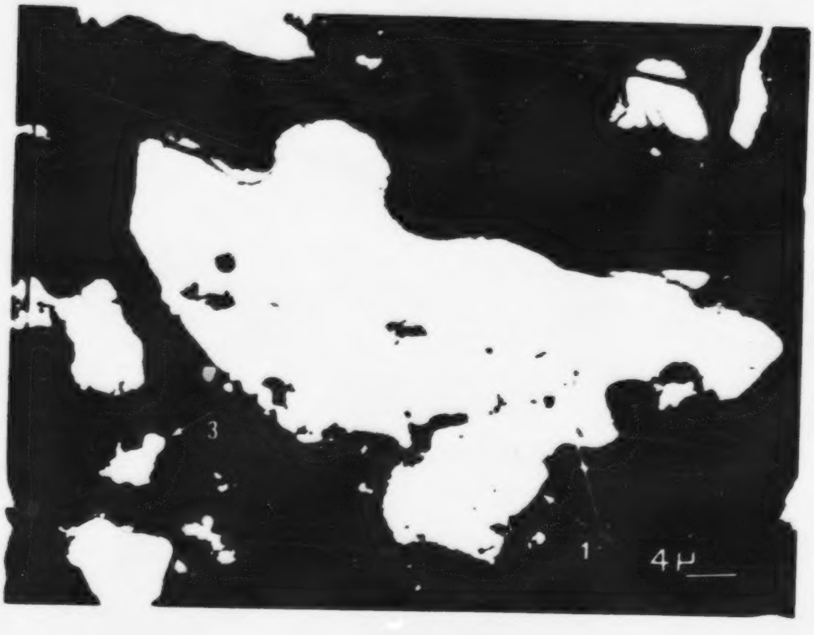

Fig. 20 - Backscattered electron micrograph of a sphalerite grain with silver sulphide inclusions (polished section mount). 1 - Ag_2S, 2 - sphalerite, 3 - $PbSO_4$.

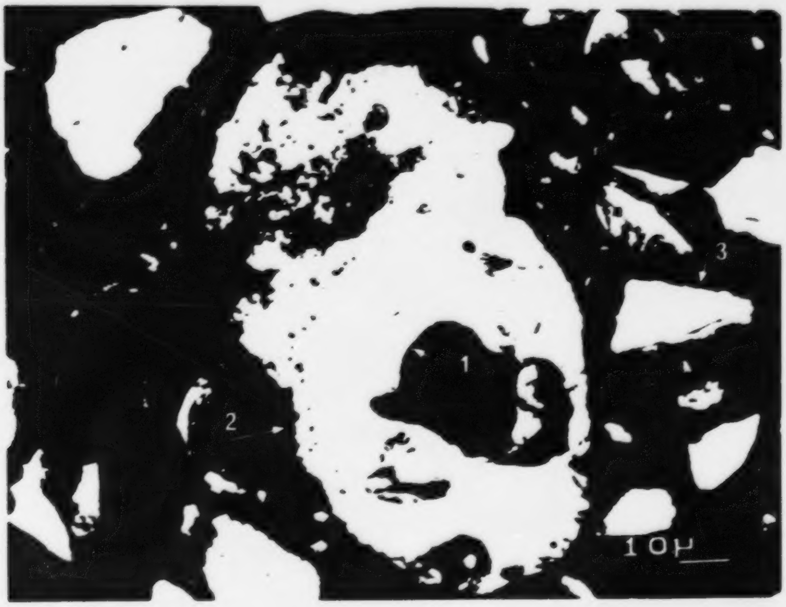

Fig. 21 - Backscattered electron micrograph of a grain of copper oxide rimmed by a Cu-Ag-S-Cl phase (polished section mount). 1 - copper oxide, 2 - Cu-Ag-S-Cl phase, 3 - sphalerite.

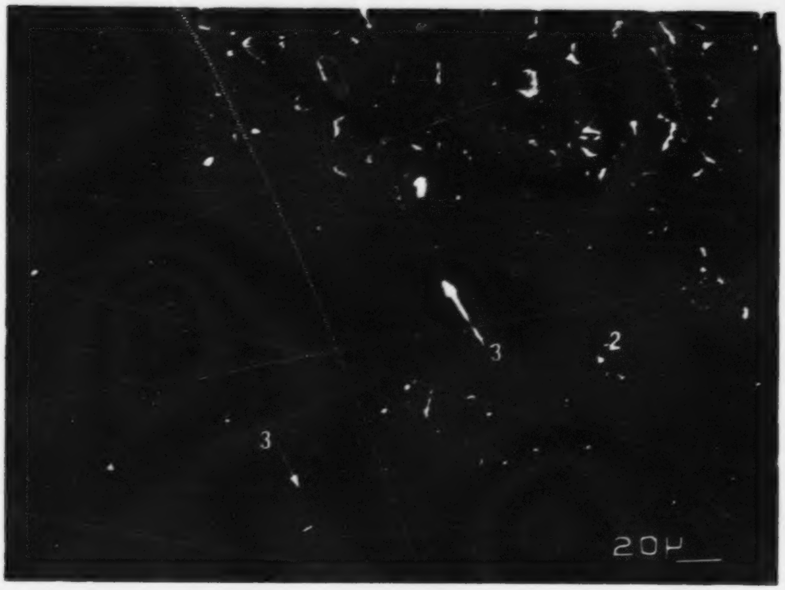

Fig. 22 - Backscattered electron micrograph presenting a general view of the low-silver flotation concentrate (polished section mount). 1 - sphalerite, 2 - $ZnFe_2O_4$, 3 - rim of $ZnFe_2O_4$.

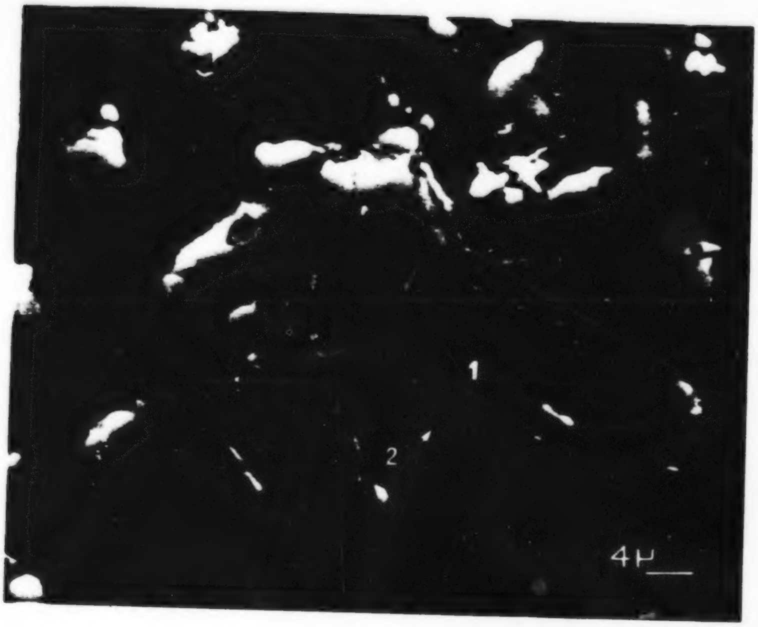

Fig. 23 - Secondary electron micrograph illustrating the zinc ferrite rim on a corroded sphalerite grain in the locked-cycle flotation concentrate (polished section mount). 1 - sphalerite, 2 - $ZnFe_2O_4$.

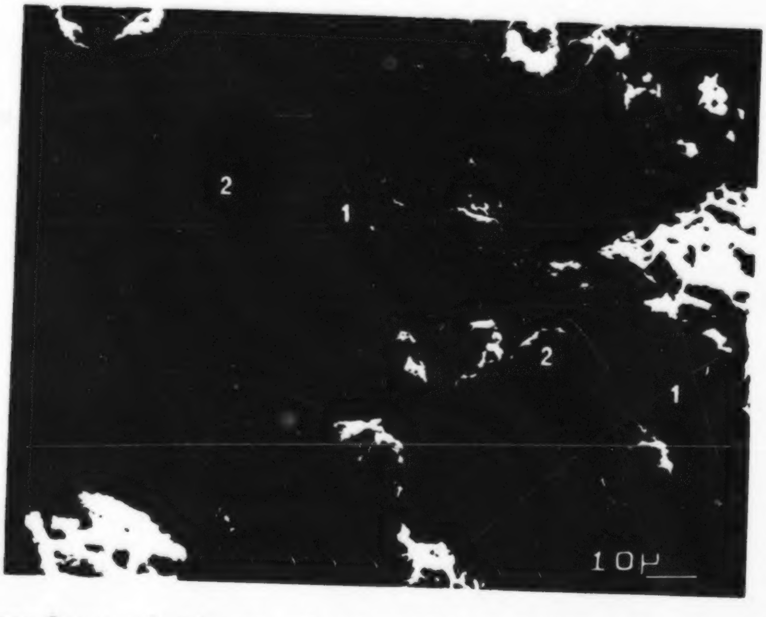

Fig. 24 - Secondary electron micrograph showing the morphology of the low-silver flotation concentrate made in the batch test (loose powder mount). 1 - sphalerite, 2 - sphalerite grains entirely rimmed by $ZnFe_2O_4$.

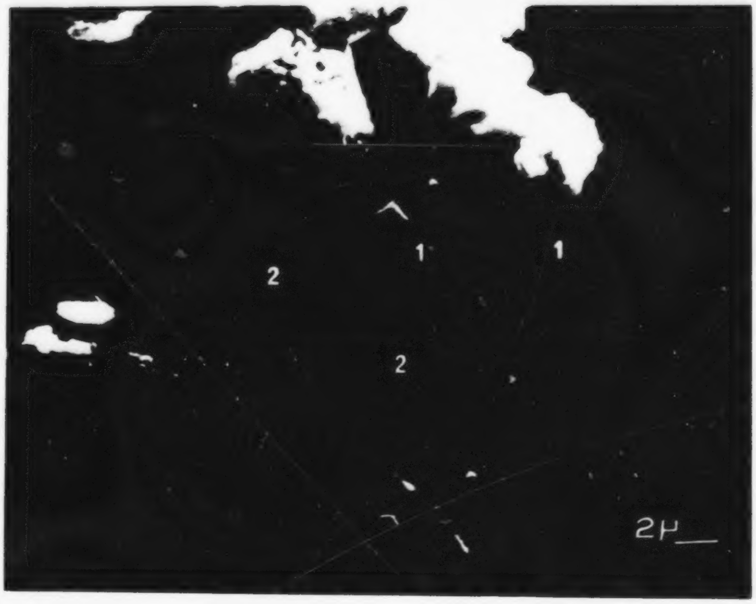

Fig. 25 - Secondary electron micrograph of several compact $ZnFe_2O_4$ grains in the low-silver flotation concentrate (loose powder mount). 1 - $ZnFe_2O_4$, 2 - sphalerite.

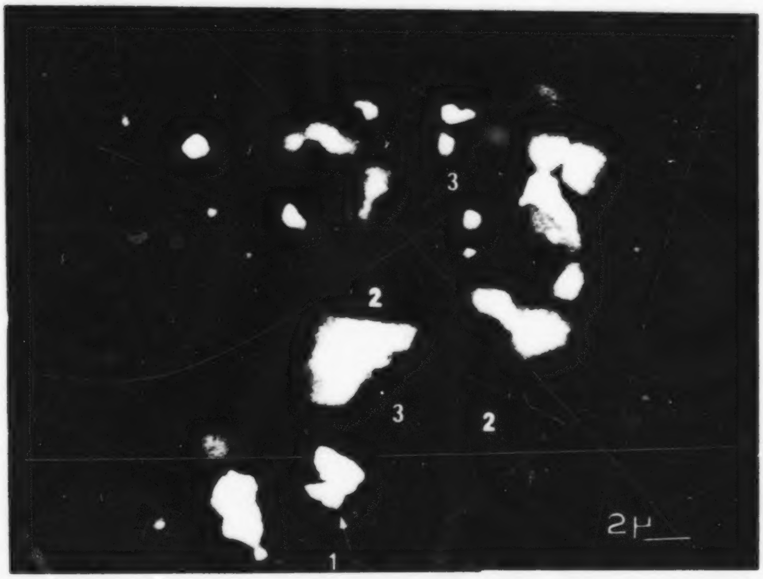

Fig. 26 - Backscattered electron micrograph illustrating several $PbSO_4$ grains associated with sphalerite and sulphur (loose powder mount). 1 - $PbSO_4$, 2 - sphalerite, 3 - elemental sulphur.

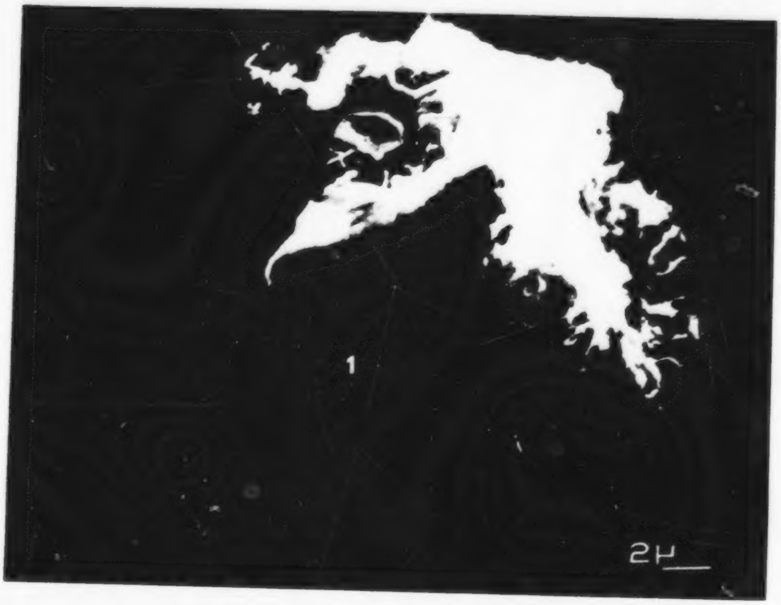

Fig. 27 - Secondary electron micrograph of a large sulphur coated sphalerite particle (loose powder mount). 1 - sulphur coated sphalerite, 2 - $ZnFe_2O_4$.

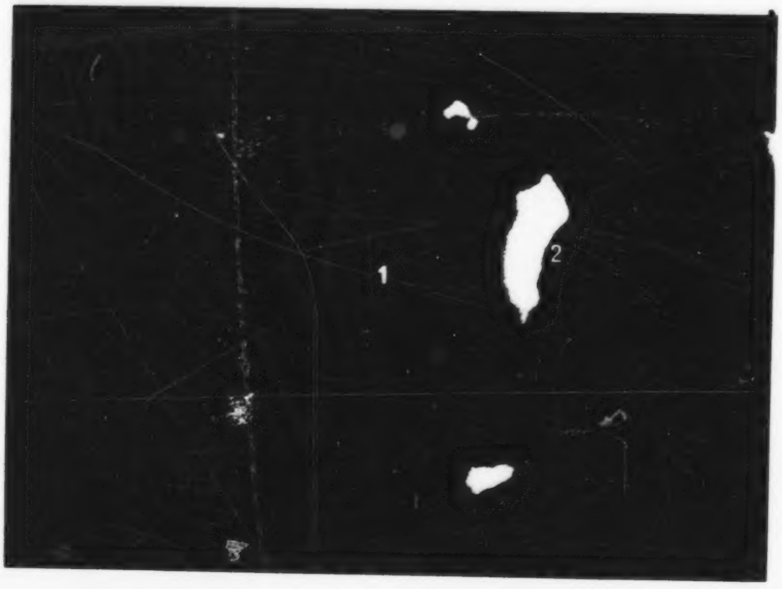

Fig. 28 - Backscattered electron micrograph of a low-iron sphalerite grain partly rimmed by Ag_2S (polished section mount). 1 - sphalerite, 2 - Ag_2S.

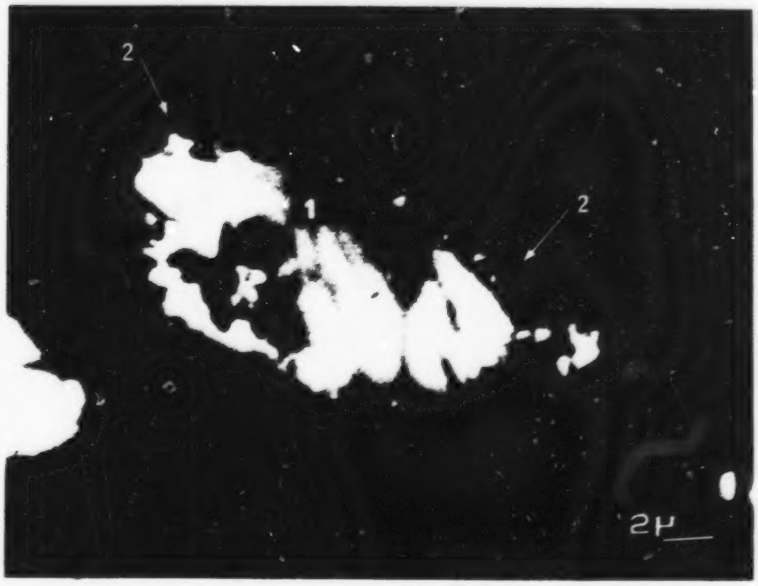

Fig. 29a - Backscattered electron micrograph of a sphalerite grain partly rimmed by Ag_2S (polished section mount). 1 - sphalerite, 2 - Ag_2S.

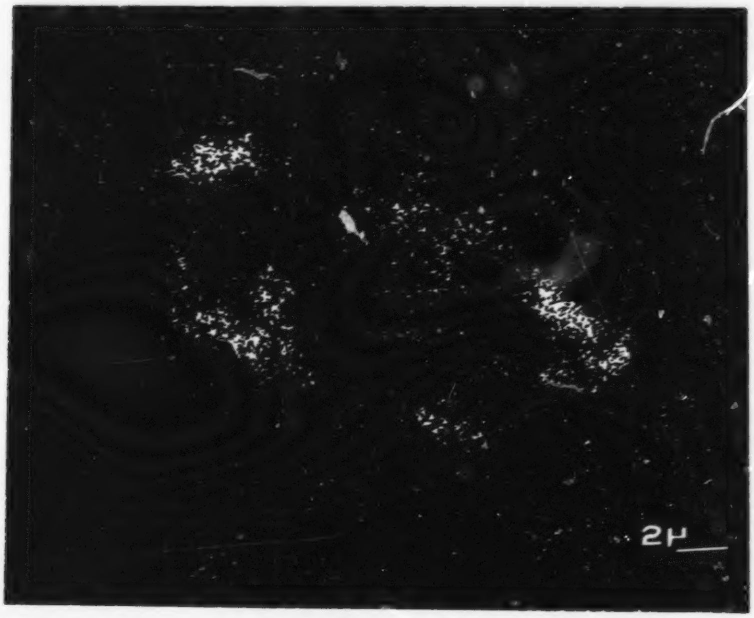

Fig. 29b - Ag Lα X-ray map of Fig. 29a that illustrates the extent of silver rimming of the sphalerite.

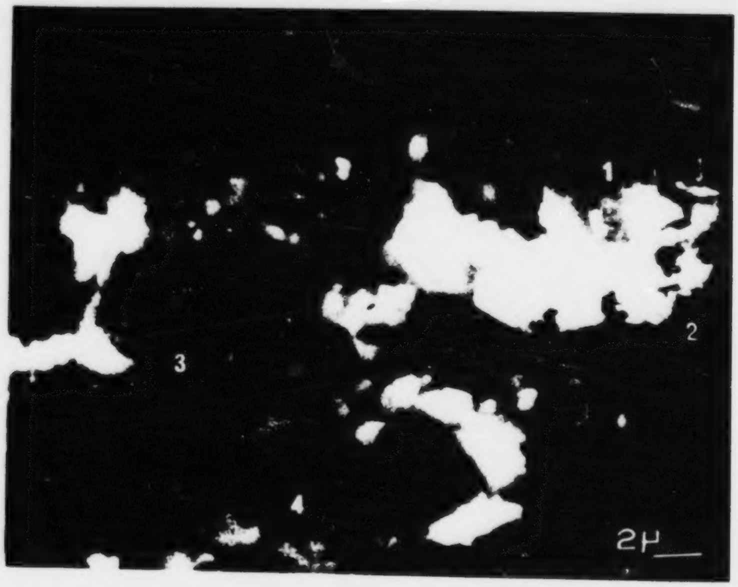

Fig. 30 - Backscattered electron micrograph of a silver-rimmed sphalerite particle (loose powder mount). 1 - sphalerite, 2 - Ag_2S, 3 - Zn-Fe sulphate, 4 - $ZnFe_2O_4$ covered sphalerite.

Fig. 31 - Backscattered electron micrograph of a sphalerite grain with isolated Ag_2S grains at various sites on the surface (polished section mount). 1 - sphalerite, 2 - Ag_2S.

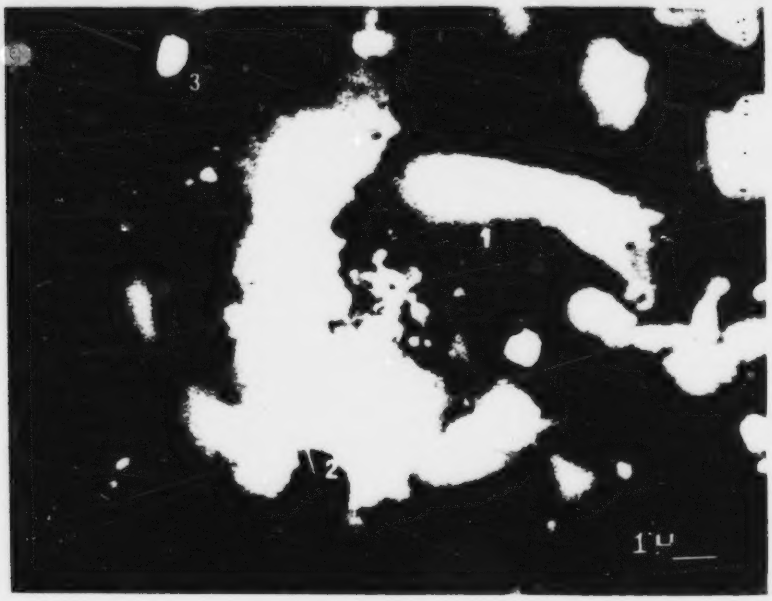

Fig. 32a - Backscattered electron micrograph of a porous mass of Ag_2S on corroded sphalerite (loose powder mount). 1 - sphalerite, 2 - Ag_2S grains, 3 - $PbSO_4$.

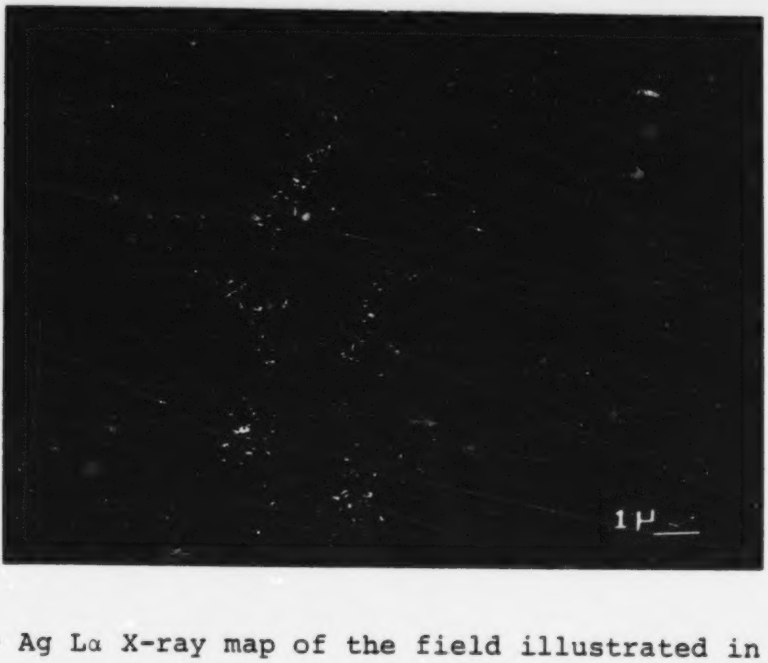

Fig. 32b - Ag Lα X-ray map of the field illustrated in Fig. 32a.

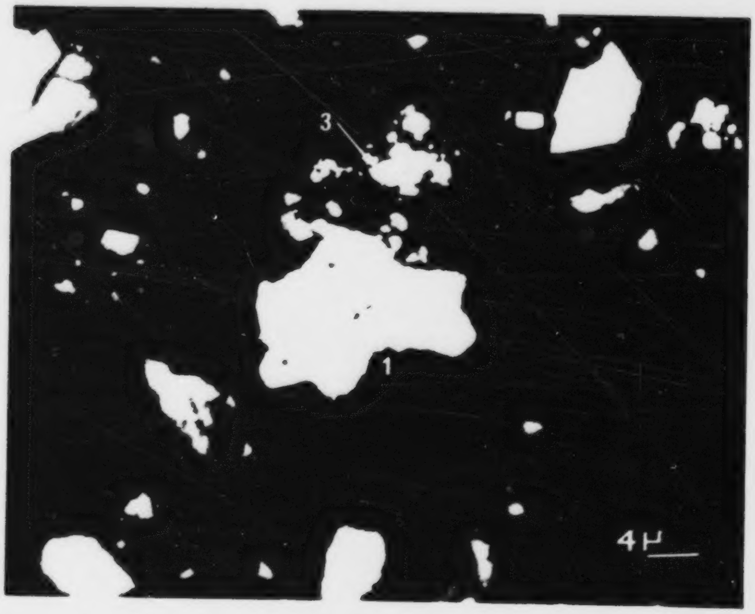

Fig. 33 - Backscattered electron micrograph of a free Ag_2S grain in the locked-cycle flotation concentrate (polished section mount). 1 - Ag_2S, 2 - sphalerite, 3 - $ZnFe_2O_4$.

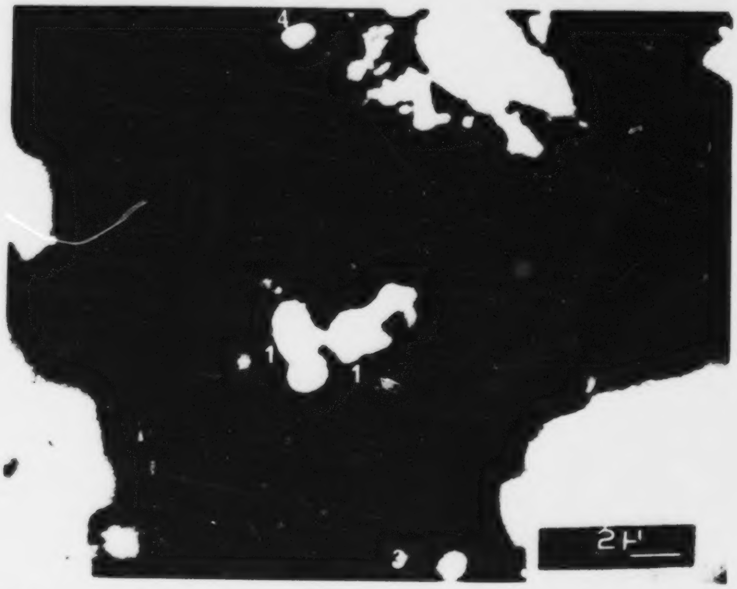

Fig. 34 - Backscattered electron micrograph of an Ag_2S cluster present in the batch flotation concentrate (polished section mount). 1 - Ag_2S, 2 - sphalerite, 3 - $ZnFe_2O_4$, 4 - $PbSO_4$.

Fig. 35a - Backscattered electron micrograph of a mass of silver-containing sulphur-silica gel present in the locked-cycle flotation concentrate (polished section mount). 1 - sulphur-silica gel, 2 - sphalerite, 3 - $ZnFe_2O_4$, 4 - $PbSO_4$.

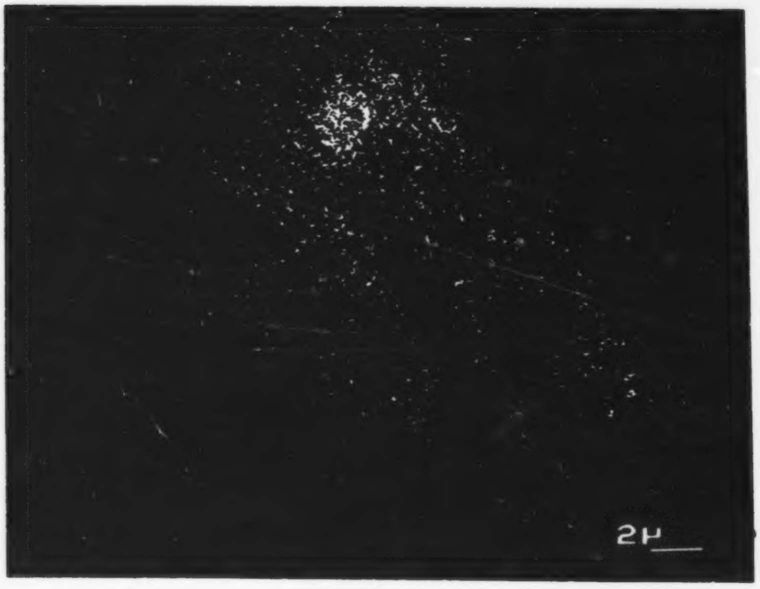

Fig. 35b - Ag Lα X-ray map of the sulphur-silica gel mass of Fig. 35a.

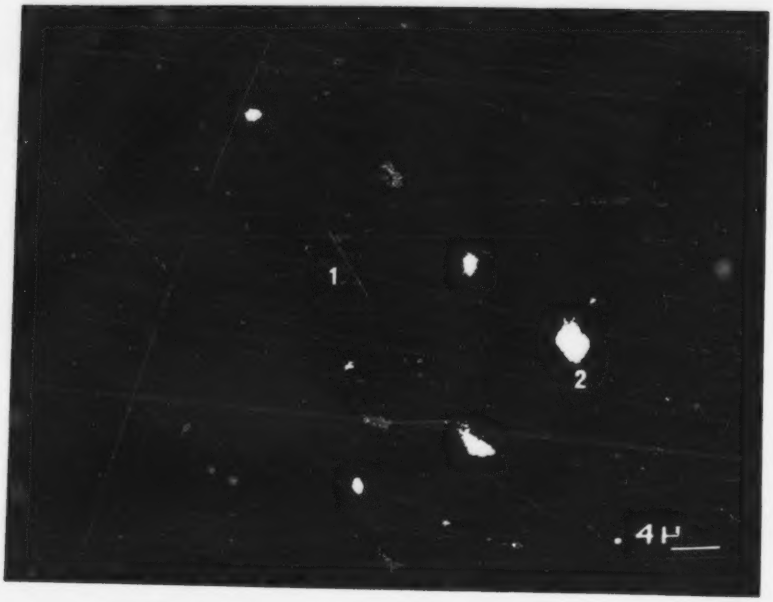

Fig. 36 - High resolution backscattered electron micrograph which shows tiny Ag_2S inclusions in the sulphur-silica gel masses such as that illustrated in Fig. 35a (polished section mount). 1 - sulphur-silica gel, 2 - Ag_2S.

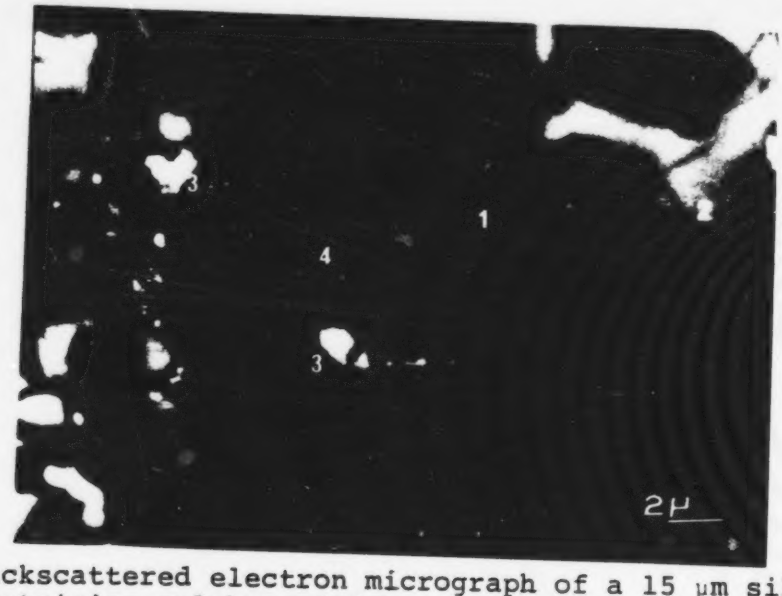

Fig. 37 - Backscattered electron micrograph of a 15 μm silver-containing sulphur-silica gel mass in the locked-cycle concentrate (polished section mount). 1 - sulphur-silica gel, 2 - sphalerite, 3 - $PbSO_4$, 4 - $ZnFe_2O_4$.

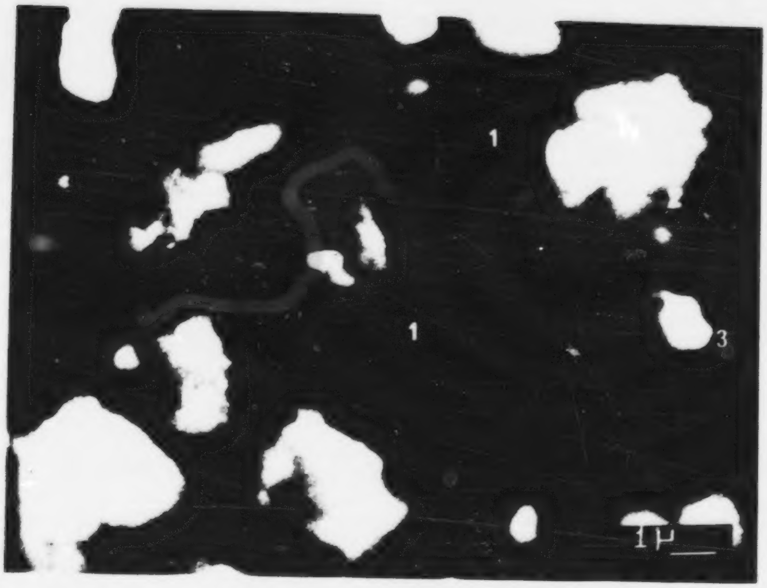

Fig. 38 - Backscattered electron micrograph of a mass of tiny sphalerite particles agglomerated by silver-containing silica gel-sulphur (loose powder mount). 1 - sulphur-silica gel, 2 - sphalerite, 3 - $PbSO_4$.

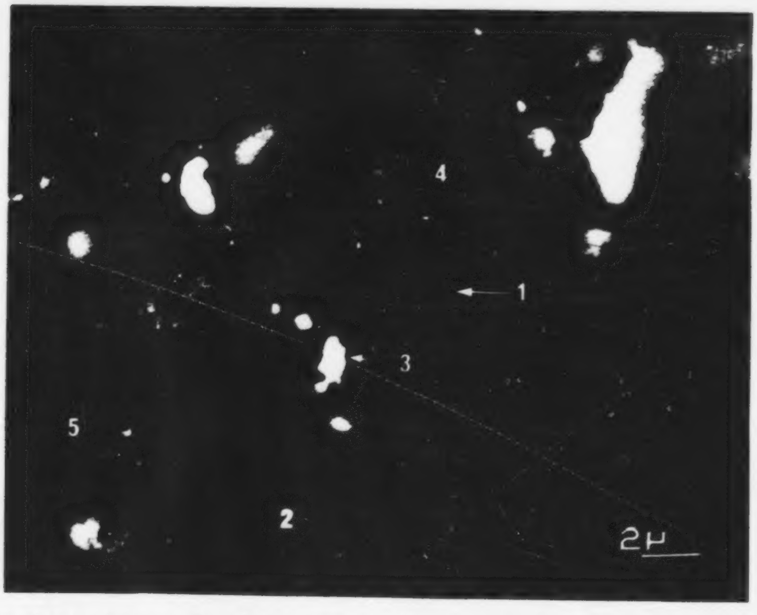

Fig. 39 - Backscattered electron micrograph of a precipitated silver-bearing CuS particle in the locked-cycle test concentrate (polished section mount). 1 - Ag-bearing CuS, 2 - sphalerite, 3 - $PbSO_4$, 4 - Ag-bearing sulphur-silica gel, 5 - $ZnFe_2O_4$.

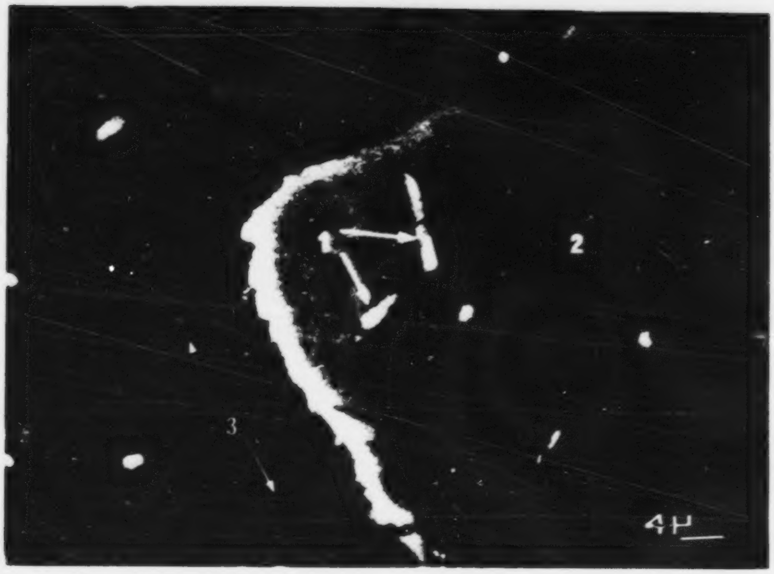

Fig. 40 - Backscattered electron micrograph of several $(Cu,Ag)_2S$ inclusions in sphalerite (polished section mount). 1 - $(Cu,Ag)_2S$, 2 - sphalerite, 3 - Ag-bearing sulphur-silica gel.